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A REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.

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In a previous article[1] one of us, together with Messrs. Hopkins and Walker, described certain experiments on the reduction of permanganic acid by precipitated manganese peroxide. It was there concluded that, whenever the latter is introduced into, or is formed in the presence of, the former or its salts, a reduction of the acid occurs with an evolution of three-fifths of its active oxygen, in accordance with the following equation:

$$x\mathrm{MnO_2} + 2\mathrm{HMnO_4} = (x+2)\mathrm{MnO_2} + \mathrm{H_2O} + 3\mathrm{O}.$$

It was also shown that to this cause is to be ascribed the observed instability of solutions of permanganate.

Six months later[2] there appeared an article by Messrs. V. Meyer and Max Von Recklinghausen in which is described the evolution of oxygen which takes place when hydrogen or carbon monoxide is absorbed by a nearly saturated (5 per cent.) acidified solution of potassium permanganate. The opinion was then expressed by one of us[3] that the phenomenon observed by Messrs. Meyer and Von Recklinghausen was

[1] This JOURNAL, 18, 401. [2] Ber. d. chem. Ges., 29, 2549.
[3] *Ibid.*, 30, 48.

due to the peroxide which is formed when reducing gases are absorbed by permanganic acid; in other words, that it is an instance of a kind of reaction which had been under observation in this laboratory for several years.

After the communication referred to had left the hands of the author, but before it appeared in printed form, an article by Messrs. H. Hirtz and V. Meyer was published[1] in which they maintain that the phenomenon observed by Messrs. Meyer and Von Recklinghausen is fundamentally different from that described by Morse, Hopkins, and Walker. The grounds for this opinion appear to be twofold. In the first place the authors make the wholly unwarranted assumption that Morse, Hopkins, and Walker experimented with *neutral* solutions only, that is, with potassium permanganate; while Messrs. Meyer and Von Recklinghausen employed *acidified* solutions. We cannot interpret otherwise the expressions: "Diese Forscher haben gefunden dass eine Loesung von uebermangansaurem Kali unter gewissen Bedingungen durch fein vertheilten Braunstein unter Entwickelung von Sauerstoff zersetzt wird." * * * "Da nämlich Wasserstoff und Kohlenoxyd als reducirende Koerper aus der Loesung der uebermangansäure Braunstein ausscheiden, und dieser, nach den genannten Autoren, mit Kaliumpermanganat Sauerstoff unter gewissen Bedingungen entwickeln kann." * * * "Ob nun die Morse-Hopkins-Walker'sche Erscheinung bei unseren *Säure*-loesungen eintrete." * * * How erroneous must have been the view which we ascribe to Messrs. Hirtz and Meyer, on the basis of the above quotations, will appear when we state that, of the 48 experiments described by Morse, Hopkins, and Walker, 35 were with *acidified* solutions of permanganate.

The second ground which the authors have for believing that the evolution of oxygen observed by them is not due to the action of the oxide on the permanganic acid, is one of great weight, but, to our minds, it is by no means conclusive. They found that when hydrogen, or carbon monoxide, is absorbed by a 5 per cent. solution of potassium permanganate to which has been added 2.5 volume-per cent. of concentrated

[1] Ber. d. chem. Ges., 29, 2828.

sulphuric acid, the evolution of oxygen which occurs *during the absorption* is much more rapid than that which takes place *after the exhaustion* of the gas. This was shown in the following manner: 20 cc. of the acidified permanganate solution and 40 cc. of hydrogen were inclosed in a glass tube and agitated together for twenty-four hours. The tube was then opened and the gas in it displaced by carbon dioxide. On closing the tube again and agitating the contents for another twenty-four hours it was found that only 2.5 cc. of oxygen had been liberated, whereas, according to the experience of Messrs. Meyer and Von Recklinghausen, about 20 cc. of oxygen are evolved when, under similar conditions, 20 cc. of the permanganate solution and 40 cc. of hydrogen are agitated for the same length of time, or even for a shorter time.

It is clear then—and our own results, to be given hereafter, confirm the conclusion—that the evolution of oxygen, which occurs when a gaseous reducing-agent is being absorbed by a concentrated acidified solution of permanganate, is much more rapid than that produced by the oxide, which results from the absorption after the gas has disappeared. It is also more rapid than that observed when an equivalent amount of oxide is produced in the permanganic acid by a liquid reducing-agent, like a solution of manganous sulphate. To us, however, the conclusion that the evolution of oxygen in the two cases is due to wholly different causes is not obvious. We should suspect, rather, that the great initial evolution, observed when hydrogen and carbon monoxide are absorbed, is in some way dependent on the *gaseous* character of these reducing-agents.

We know at present altogether too little regarding the reduction of permanganic acid by the peroxide to give an opinion of any value as to its cause; and we attach very little value to present speculations on the subject, except so far as they may prove useful in giving direction to a further study of the phenomenon. There is, however, one fact which suggests a provisional hypothesis. We have considerable evidence tending to show that the molecules of the ordinary precipitated peroxides of manganese are quite complex. Perhaps the best evidence of this is to be found in the large

formulas which must be assigned to them in view of the small proportions of water, or of alkalies or other bases which they contain. If they are thus complex, it is conceivable that the tendency toward increasing complexity of constitution should be strong enough to effect the decomposition of permanganic acid with liberation of the superfluous oxygen.

If, in the absence of any other explanation of the reduction of permanganic acid by the peroxide, we accept for the moment the proposed hypothesis, we should ascribe the greater initial evolution of oxygen which is observed when gaseous reducing-agents are used, to the greater initial simplicity of the precipitated peroxide molecules. It is interesting in this connection to notice the volume-relations of the hydrogen absorbed and the oxygen which is liberated during or immediately following the absorption. They are approximately 2 : 1 in all of the experiments of Meyer and Von Recklinghausen. This relation would be explained in terms of the suggested hypothesis by the following reactions :

$$2HMnO_4 + 3H_2 = 4H_2O + 2MnO_2;$$
$$2MnO_2 + 2HMnO_4 = H_2O + 2(MnO_2)_2 + 1\tfrac{1}{2}O_2.$$

We wish to state again that we have but little confidence in the above speculations. We claim for them this merit only, that, inherently, they are not less improbable than the supposition that the evolution of free oxygen in the two cases under consideration is due to entirely distinct and different causes.

Furthermore, we do not see that the problem can be solved by any simple experimental demonstration. The "experimentum crusis" of Messrs. Hirtz and Meyer[1] established but one thing; namely, the fact that the evolution of oxygen is phenomenally rapid during or immediately subsequent to the precipitation of the peroxide, when a gaseous reducing-agent is employed, and that fact, taken alone, appears to throw no light on the cause of the evolution. Convinced that, with our slight basis of established fact, discussion is premature, if not profitless, we have undertaken a further study of the reduction of permanganic acid by manganese peroxide. The

[1] Ber. d. chem. Ges., **29**, 2829.

present communication contains the results which were obtained on treating the acid, under equal conditions, with equivalent quantities of hydrogen gas and manganous sulphate. We have thus far experimented with three concentrations of permanganate solution.

The first (A) contained in 1 cc. 2.822 milligrams of $KMnO_4$, equivalent to 5 milligrams of iron. The second (B) was twice as concentrated as A. The third (C) contained in each cc. 51 milligrams of $KMnO_4$, equivalent to 90.38 milligrams of iron. The solutions A and B are of the concentration usually employed in analytical work, while C has about the strength of the 5 per cent. solution which was employed by Messrs. Meyer and Von Recklinghausen and later by Messrs. Hirtz and Meyer.

Great pains were taken to free these solutions from the oxide which is usually found in the commercial salt, and which, as has been shown, is the usual cause of the instability of unfiltered solutions of potassium permanganate. To this end compact asbestos filters were prepared upon perforated porcelain disks placed in the bottom of cylindrical funnels, such as are used in the Gooch method of filtration. Two filters, one placed above the other, were employed. The lower one was closed with a perforated stopper through which the stem of the upper one passed. The filter through which the liquid entered the flask was thus protected from the dust of the air, and the absence of any brown coloration of the lower filter proved the effectiveness of the filtration. We have found these precautions necessary in all quantitative experiments on the reduction of permanganic acid by the peroxide; since, if they are neglected, it is impossible to ascertain how much of the observed reduction is to be ascribed to the oxide purposely added, and how much to that which was already in the solution.

When solutions of permanganate which contain suspended oxide are heated—especially those which have been acidified—the quantity of the oxide increases very rapidly. We call attention to this fact in connection with the necessity for careful filtration, because it appears to us to have a bearing on some of the results which were obtained by Messrs. Meyer

and Von Recklinghausen. Their acidified solutions were "gut ausgekocht," but it does not appear from their published account that they were filtered.

The volume of permanganate solution used was the same in all experiments; namely, 20 cc. This quantity was enclosed with whatever was to be added to it, in tubes having about 80 cc. capacity, except in the case of solution C, where, owing to the large volume of hydrogen used in some experiments, larger tubes were employed.

Our agitating arrangement was an oscillating table upon which the tubes were held by rawhide lacings. The table was rocked by means of an electric motor and made about 100 strokes per minute. The agitation was continuous, except for occasional interruptions which lasted only a few minutes.

The amount of reduction effected during the agitation was measured by means of standard solutions of oxalic acid and potassium permanganate. This method, with the use of calibrated measuring apparatus, appeared to us quite as accurate as that of determining directly the volume of the liberated oxygen.

Messrs. Meyer and Von Recklinghausen found that when 20 cc. quantities of their 5 per cent. acidified solution of permanganate were agitated with air in closed tubes, they obtained volumes of oxygen ranging from 1.9 to 2.9 cc. An agitation of thirty-three and a half hours gave them 1.9 and 2.2 cc., while in a parallel experiment in which the agitation was continued for eighty-seven hours they obtained only 2.4 cc. In another instance the volumes of liberated oxygen were, at the end of thirty-three and a half hours, 2.8 and 2.9 cc., and at the end of eighty-seven hours, 2.4 cc. Since the decomposition was not appreciably greater in eighty-seven than in thirty-three and a half hours, the authors were led to believe that there is a limit to the reaction by which the oxygen is liberated. These results were not in accord with our own experience. In the first place, we have always found dilute, moderately acidified solutions of permanganate quite stable at ordinary temperatures, provided they were free from oxide. In the second place, in all the cases which have come

under our observation, the decomposition of permanganic acid by the peroxide, which is attended by the liberation of oxygen, has been a continuous reaction, which ceased only when all of the acid had been reduced to the oxide. We had not, however, experimented with solutions as concentrated as that used by Messrs. Meyer and Von Recklinghausen. We therefore inclosed in glass tubes of about 80 cc. capacity 20 cc. portions of permanganate solution C. (51 milligrams of $KMnO_4$ per cc.) and volumes of diluted sulphuric acid, which were equivalent to three times the potassium of the salt. These were agitated for twenty-four hours and then titrated with oxalic acid. The reduction, if any had taken place, was too minute to be detected, nor was any trace of a brown deposit upon the glass to be discovered. The degree of acidity was somewhat greater in our solution than in that employed by Messrs. Meyer and Von Recklinghausen. The difference in the results we must ascribe to the absence of oxide from our solution, and the presence of it in theirs. Their 5 per cent. solution of permanganate was acidified with *concentrated* acid, and then boiled ("gut ausgekocht"), but it does not appear to have been filtered. This treatment leads infallibly to the formation of a large quantity of the oxide; for, when strong sulphuric acid is added to a 5 per cent. solution of the salt, there is a visible precipitation of the peroxide, and the quantity of it is rapidly increased by heating the solution to the boiling-point. Our solution, on the other hand, was filtered with great care, and acidified with diluted acid (3 parts of water to 1 of acid). Moreover, great pains were taken in cleansing the tubes, and to prevent the entrance into them of dust, or any reducing substance.

Having failed to establish the fact of decomposition within twenty-four hour periods, we determined to extend the time of agitation, using varying proportions of acid; and to compare the more dilute solutions A and B with C with respect to stability. The results and the conditions under which they were obtained, are given in tabular form. The numbers given under the head of "volume reduced" signify reduction in accordance with the equation, $2HMnO_4 = H_2O + 2MnO_2 + 3O$, and not total reduction of the permanganic acid.

Permanganate Solution A; 1 cc. = 5 Milligrams Fe.

Acid.	Time. Hours.	Volume reduced. cc.	Oxygen lost. cc.
O	300	0.12	0.06
O	"	0.11	0.05
= K	"	0.11	0.05
= K	"	0.06	0.03
= 2K	"	0.20	0.10
= 2K	"	0.10	0.05

Permanganate Solution B; 1 cc. = 10 Milligrams Fe.

Acid.	Time. Hours.	Volume reduced. cc.	Oxygen lost. cc.
O	150	0.02	0.02
O	"	0.04	0.04
= 3K	"	0.10	0.10
= 3K	"	0.10	0.10
= 6K	"	0.08	0.08
= 6K	"	0.10	0.10

Permanganate Solution C; 5 per cent. $KMnO_4$.

Acid.	Time. Hours.	Volume reduced. cc.	Oxygen lost. cc.
O	150	0.00	0.00
O	"	0.00	0.00
= K	"	0.05	0.45
= K	"	0.04	0.36
= 2K	"	0.02	0.18
= 2K	"	0.11	0.99
= 3K	"	0.40	3.61
= 3K	"	0.22	1.91

It will be seen that none of the three solutions in the neutral condition lost a measurable quantity of oxygen. As regards the acidified solutions, it appears that A and B suffered but little if any decomposition, whether the acid was equivalent to once or six times the potassium of the permanganate. In the case of those acidified portions of the solution C, in which the acid was equivalent to three times the potassium of the permanganate, there was, after an agitation of one hundred and fifty hours, some evidence of decomposition. A slight deposit of the brown oxide could be detected upon the glass. This evidence of reduction was wanting in those instances in which the acid was equivalent to once and twice the potassium.

If we succeeded in our endeavor wholly to exclude the oxide from our solutions, it must be concluded that a 5 per cent. solution of permanganate becomes *per se* somewhat unstable when treated with a quantity of sulphuric acid which is equivalent to three times the potassium of the salt. Our solution C, however, proves itself much more stable than the equally concentrated, but somewhat less acid, solution of Messrs. Meyer and Von Recklinghausen. The most obvious cause of this difference we have already referred to; namely, the certain presence of suspended oxide in their solution at the beginning of the agitation.

We shall not attempt to explain the fact that Messrs. Meyer and Von Recklinghausen obtained no larger volumes of oxygen after an agitation of eighty-seven hours than were liberated in other experiments during thirty-three and a half hours; but it occurs to us as something which may have a bearing on the case, that unless proper precautions were taken at the time of transferring the liquid to the tubes, to secure a uniform distribution of all the suspended and precipitated oxide, the quantities of oxide introduced into the different tubes would be likely to vary. That the liberation of oxygen, which occurs when an acidified solution of permanganate containing suspended oxide, is agitated in closed tubes, *does not* cease after a few hours will be amply proved by our later experiments.

The next series of experiments was designed to determine the relative rates of reduction when equal volumes of permanganic acid are agitated: on the one hand, with a given volume of hydrogen; and on the other, with a quantity of the peroxide which is equal to that which should be produced by the absorption of the hydrogen. Here again, the three solutions, A, B, and C, were employed in the comparison.

The quantities of permanganate to be reduced were in all cases 20 cc. In addition to this, there was added to the hydrogen tubes a quantity of permanganate which would dispose of the gas in accordance with the equation,

$$HMnO_4 + 3H = 2H_2O + MnO_2,$$

and to the other tubes, enough permanganate and manganous

sulphate to produce the same amount of oxide as would result from the absorption of the hydrogen, according to the equation,

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 2HKSO_4 + H_2SO_4 + 5MnO_2.$$

In adding the acid, account was taken of the fact that, in the case of those tubes in which the peroxide was produced by the action of the manganous salt on the permanganate, a portion of the required acid had already been introduced through the sulphate.

In order that the quantity of the gas introduced might be accurately measured, the tubes designed to receive the hydrogen were drawn out, at one end to a capillary and at the other to a narrow neck, just wide enough to permit the introduction of liquids from a burette. After introducing the permanganate and the calculated amount of sulphuric acid, the larger passage was closed before the blast-lamp. The capillary end was then attached to a Hempel burette filled with mercury, and a volume of air was withdrawn from the tube which was equal to that of the hydrogen to be introduced. The burette was then replaced by one containing hydrogen. By careful manipulation no especial difficulty was experienced in introducing quite exactly the required volume of gas. To prevent the possibility of an explosion of the mixture of gases while closing the capillary, the tube was so inclined during the operation, that the liquid in the tube covered the inner end of the narrow passage. It is hardly necessary to state that, in estimating the volume of gas required for an experiment, proper corrections were made for temperature, pressure, and water vapor.

Through the addition of sulphuric acid to all of the tubes, and of a standard solution of manganous sulphate to a portion of them, the original permanganate solutions were somewhat diluted, and those portions to which the manganous sulphate was added, to a greater extent than the others; hence, in order to equalize the conditions as to concentration, it was necessary to introduce a certain amount of water into the tubes in which the permanganate was to be agitated with hydrogen.

The tables which follow give the molecular ratio of the permanganic acid to be reduced to the oxide, the relation of the acid to the potassium of the permanganate, the time of agitation, the percentage reduction of the acid to peroxide, and the volumes of oxygen which were estimated to have been lost.

Permanganate Solution A.

1 cc. equivalent to 5 milligrams of iron.

Volume of original solution to be reduced = 20 cc.

Volumes of hydrogen used = 7.5 cc.

Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12.5$.

Acid.	Time. Hours.	Decomposition by MnO_2 from $MnSO_4$. Per cent.	Volume of oxygen liberated. cc.	Decomposition by MnO_2 from H_2. Per cent.	Volume of oxygen liberated. cc.
K	150	13.75	0.83	9.59	0.58
K	150	16.50	0.99	8.55	0.51
K	300	21.67	1.29	10.25	0.62
K	600	40.00	2.40	14.34	0.86
2K	150	21.35	1.28	11.60	0.70
2K	150	17.65	1.06	14.00	0.74
2K	300	28.33	1.70	17.00	1.02
2K	300	28.33	1.70	16.67	1.00
2K	600	41.66	2.50	21.08	1.27
3K	150	15.16	0.91	15.83	0.95
3K	150	14.67	0.88	13.50	0.81
3K	300	26.34	1.58	20.83	1.25
3K	300	23.90	1.43	20.74	1.25
3K	600	44.91	2.70	27.00	1.62
3K	24	6.67	0.40	hydrogen not all absorbed.	....
3K	24	5.25	0.32	"	....

It should be remarked with regard to the above, as well as all following similar data that, of the figures expressing reduction of permanganic acid, only those on the same horizontal line are safely comparable. This is true even when the time of agitation is the same in successive experiments, unless the agitation happened to be simultaneous. The rate of the reduction appears to be influenced even by such changes of temperature as are experienced in the laboratory, as, for instance, between day and night.

Permanganate Solution B.

1 cc. equivalent to 10 milligrams of iron.
Volume of original solution to be reduced = 20 cc.
Volumes of hydrogen used = 15 cc.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12.5$.

Acid.	Time. Hours.	Decomposition by MnO_2 from $MnSO_4$. Per cent.	Volume of oxygen liberated. cc.	Decomposition by MnO_2 from H_2. Per cent.	Volume of oxygen liberated. cc.
3K	150	17.5	2.1	28.25	3.39
3K	150	15.08	1.81	27.33	3.21
3K	150	17.17	2.06	28.25	3.39
3K	300	33.17	3.98	31.75	3.80
3K	300	32.93	3.95	32.68	3.92
3K	600	61.59	7.38	43.75	5.25
3K	600	62.50	7.50	41.83	5.02
6K	150	18.18	2.18	32.50	3.90
6K	150	19.34	2.32	31.83	3.82
6K	150	20.18	2.42	35.08	4.21
6K	300	31.75	3.81	36.00	4.31
6K	300	31.75	3.81	37.08	4.45
6K	600	60.75	7.28	44.00	5.29
6K	600	75.75	9.08	46.43	5.57
3K	24	3.33	0.40	8.58	1.03
3K	24	4.00	0.48	10.67	1.28

Permanganate Solution C.

1 cc. contained 51 milligrams $KMnO_4 = 89.38$ milligrams Fe.
Volume of original solution to be reduced = 20 cc.
Volumes of hydrogen used = 40 cc.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 3.784$.

Acid.	Time. Hours.	Decomposition by MnO_2 from $MnSO_4$. Per cent.	Volume of oxygen liberated. cc.	Decomposition by MnO_2 from H_2. Per cent.	Volume of oxygen liberated. cc.
K	150	9.68	10.48	19.93	21.58
K	150	13.75	14.90	19.93	21.58
K	300	22.50	24.38	21.58	23.39
K	300	17.00	18.42	21.75	23.57
2K	150	11.83	12.82	22.50	24.38
2K	150	12.68	13.73	23.93	25.92
2K	300	16.65	18.06	22.08	23.93
2K	300	20.93	22.66	23.33	25.28
3K	150	13.50	14.63	23.74	25.74
3K	150	12.93	14.00	25.83	27.99
3K	300	17.75	19.23	26.75	28.90
3K	24	2.50	2.71	19.58	21.22
3K	24	2.50	2.71	20.18	22.85

The relation of the reduction of the permanganic acid to the time of agitation, as well as to the acidity of the solutions, will be made clearer by the following arrangement, in which the means are given in the case of duplicated determinations:

Solution A.

1. Oxide from $MnSO_4$.

	24 hours. Per cent.	150 hours. Per cent.	300 hours. Per cent.	600 hours. Per cent.
Acid = K	....	15.13	21.67	40.00
" = 2K	....	19.50	28.33	41.66
" = 3K	5.96	14.92	25.12	44.91

2. Oxide from H_2.

Acid = K	....	9.07	10.25	14.34
" = 2K	....	12.08	16.84	21.08
" = 3K	hydrogen not all absorbed.	14.67	20.79	27.00

Solution B.

1. Oxide from $MnSO_4$.

Acid = 3K	3.67	15.56	33.05	62.00
" = 6K	....	19.23	31.75	68.27

2. Oxide from H_2.

Acid = 3K	9.63	27.94	32.22	42.79
" = 6K	....	33.14	36.54	45.22

Solution C.

1. Oxide from $MnSO_4$.

Acid = K	....	11.72	19.75	....
" = 2K	....	12.26	18.75	....
" = 3K	2.50	13.22	17.75	....

2. Oxide from H_2.

Acid = K	....	19.93	21.67	....
" = 2K	....	23.22	22.71	....
" = 3K	19.88	24.82	26.75	....

An examination of the preceding table, for the purpose of comparing the efficiency of manganous sulphate and hydrogen as oxygen liberating agents, shows that, in the case of solutions B and C, the latter is much more active than the former during the first twenty-four hours—that is, during the period

of, or immediately following, the formation of the peroxide which results from the absorption of the gas. This is apparently not true of the very dilute solution A; for in the experiments upon it, a somewhat smaller reduction of the acid was found than would have been accounted for by the complete absorption of the hydrogen. It cannot, however, be affirmed that the quantity of oxygen liberated was less, in proportion to hydrogen absorbed, in A than in B and C. This is one of the questions to which it is hoped to give further attention in the future. The maximum efficiency of the hydrogen as a quickly acting oxygen-liberating agent, appears to be reached in the case of the nearly saturated solution C, in which the mean reduction during the first twenty-four hours amounted to 19.88 per cent., as against 2.5 per cent. for the manganous sulphate. We call attention to the fact—also noticeable in the results of Messrs. Meyer and Von Recklinghausen—that the reduction of 19.88 per cent. signifies the liberation of 22 cc. of oxygen, a volume which is nearly one-half that of the hydrogen (40 cc.) employed in all the experiments with the solution C.

During the period from twenty-four to one hundred and fifty hours, the oxide produced by hydrogen acted much less rapidly in C than the oxide from the manganous salt. In B —and possibly also in A—the order of efficiency appears to be reversed, the oxide from the hydrogen being the more active one. The latter fact was interesting to us, because it may possibly throw some light upon the important question, whether the phenomenal liberation of oxygen which is observed when hydrogen, or carbon monoxide, acts upon permanganic acid, *attends the absorbtion of the gas or follows the formation of the oxide produced by the absorption of the same;* and it suggests a line of investigation which we hope to pursue.

During the period from one hundred and fifty to three hundred hours—also during that from three hundred to six hundred hours, wherever the agitation was so long continued—the oxide from the hydrogen was decidedly less active than that from the sulphate. In one instance, in which a portion

of the solution C had been agitated with hydrogen for three hundred hours, a smaller reduction was found than had occurred in similar experiments during an agitation of one hundred and fifty hours. This discrepancy was explained at the time by the low temperature which prevailed during the agitation of the tube whose contents showed the low reduction.

Assuming that liberation of oxygen in solutions of permanganate or permanganic acid is, in general, due to the presence of suspended oxide, there is no evidence to be found in our results that the reaction has a limit, as believed by Messrs. Meyer and Von Recklinghausen. The evidence to the contrary is very clear in all cases in which the suspended oxide was prepared from manganous sulphate, and also in those cases in which the oxide from hydrogen acted upon solutions A and B. The reduction accomplished in C by the oxide from hydrogen is apparently small during the twenty-four to one hundred and fifty hour and the one hundred and fifty to three hundred hour periods. It is, however, unmistakable, except in the one case which has already been explained. That the percentage reduction for equal periods of time after the first twenty-four hours should be smaller throughout in C than A and B, is easily accounted for by the fact that the suspended oxide in C was relatively less than one-third of that in A and B.

The work which we have here described is only a fragment of a proposed investigation of the reduction of permanganic acid by the peroxide of manganese. The results obtained are not decisive; nor are they even strikingly important in their direct bearing on the question of the cause of the difference between the action of gaseous and liquid reducing agents on permanganic acid. They do, however, suggest certain possible methods of solving the problem.

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May, 1898.

THE ATOMIC WEIGHT OF CADMIUM.[1]

By H. N. Morse and H. B. Arbuckle.

Having redetermined the atomic weight of zinc[2] by the method of Morse and Burton,[3] making corrections for the gas which Richards and Rogers[4] found to be retained by the oxide, even at high temperatures, we undertook a similar repetition of the work of Morse and Jones[5] on the atomic weight of cadmium, for the purpose of correcting their results, if cadmium oxide should also be found to retain gas.

Richards and Rogers found no gas in their specimens of cadmium oxide, but as their material had been heated to a higher temperature than is permissible in an atomic weight determination of this metal, we could not be certain that the oxide of Morse and Jones was likewise free from gas. Moreover, it was found by Bucher,[6] in this laboratory, that when a given weight of cadmium oxide, derived from the carbonate, is converted into nitrate, and then again into oxide, the last weight of the oxide is greater than the first. The experience of Bucher points directly to the presence of gas in the oxide from the nitrate.

Another sufficient reason for a revision of the work is to be found in the fact that the results which have been obtained by work upon the halogen salts of cadmium have been throughout notably higher than those based on the weight of the oxide. It appeared desirable to clear up, if possible, the cause of this discrepancy between the two methods.

The metal which was used in this work was the same as that employed by Morse and Jones. It was, in fact, a portion of that prepared for the earlier experiments. It had been purified by six fractional redistillations in a vacuum, and examined spectroscopically by Professor Rowland. The details of the distillation process have already been described[7] and need not be repeated.

The nitric acid with which the metal was dissolved was

[1] The work of which an account is given in this article was carried out under a grant from the Bache Fund (National Academy of Sciences).

[2] This Journal, **20**, 195.

[3] *Ibid.*, **10**, 311.

[4] Proc. Am. Acad., **28**, 200.

[5] This Journal, **14**, 261.

[6] Dissertation, 1894, 22.

[7] This Journal, **10**, 311; and **14**, 261.

prepared, as in the earlier work upon zinc and cadmium, by condensing the vapors of the acid upon the surface of a large platinum dish. 15 cc. portions of it, when evaporated in platinum, gave no visible or weighable residue. We deemed it necessary to test the latter condition with unusual care, because of the wide difference between the atomic weights of cadmium and oxygen, and the correspondingly large effect of small errors in weight of material upon the results.

The arrangement of the crucibles in which the metal was converted first into nitrate, then into oxide, and finally weighed, was the same as that formerly used for both cadmium and zinc. It consisted of a small porcelain crucible (No. oo) in which the metal was dissolved, and a larger one (No. II.) in which the smaller one was placed. The smaller, but not the larger, crucible was provided with a lid. The lid and the crucible were, however, separated by means of bent pieces of platinum wire hung over the edge of the latter, thus providing for the free escape of vapors during the solution of the metal and the conversion of the nitrate into the oxide. The glaze was removed from the bottoms of the crucibles, also from the under side of the lid, by means of hydrofluoric acid. The pair of crucibles was weighed together and never separated. A similar, but slightly lighter, pair of crucibles was prepared at the same time to serve as a counterpoise. The platinum hooks belonging to the two sets were brought to nearly equal weight by filing, and then fragments of porcelain were added to the counterpoise until the weights of the two pairs differed by only a small fraction of a milligram. Both were then heated under the same conditions for several hours. The difference between their weights was then carefully determined, after which they were again heated, in order to determine whether the difference remained constant. Throughout the entire determination the two sets of crucibles were treated as nearly alike as the purposes for which they were used would permit; for instance, if the pair in which the metal had been dissolved was heated, the tare was heated under the same conditions for the same length of time.

Owing to the volatility of cadmium oxide at high temperatures, it was necessary to give careful attention to our heating

arrangements. A small double-walled furnace was made of asbestos board. Two opposite sides were cut away near their centers to permit the entrance of blast flames, and the upper edges were notched to allow the products of combustion to escape. The bath, in which the crucibles previously described were heated, consisted of a large porcelain crucible. This was inserted in a hole in the piece of asbestos board which served as a cover to the furnace. In the bottom of the bath was placed a piece of unglazed porcelain on which the crucibles rested while being heated.

For the air-blast we had a small Root blower which was run by an electric motor; and, as the current was very constant, we were able to maintain quite uniform temperatures. The lamps which we first tried were 2 glass-blower's lamps with 2 jets each. These, with a given adjustment of air and gas-cocks, and speed of the blower, gave us a temperature in the furnace which lay between the fusing-points of sodium chloride (776°) and potassium carbonate (835°). As the former salt fused very readily, while the latter showed no signs of having been softened, we judge that the temperature must have been about 800°. At this temperature it was found practicable to reduce the oxide to constant weight. To ascertain whether a higher temperature might not be employed with safety, we substituted ordinary blast-lamps for those first selected. These gave us a temperature between the fusing-points of pure silver (960°) and potassium sulphate (1066°). But it was found that, at this temperature, specimens of oxide which had been brought to constant weight under the first arrangement began to lose in weight. That the loss was due, in part at least, to sublimation was clear from the fact that portions of the crucible previously white became tarnished with a yellow coating. The blast-lamps were therefore exchanged for those we had used in the first place, and no further change of lamps, or of gas or blast adjustments, was made during the entire work. The temperature was, however, tested from time to time, but always with the same result; sodium chloride fused readily, while potassium carbonate remained unfused after heating for an entire day.

The apparatus for the liberation, collection, and analysis of

the occluded gases was that devised for our earlier work on the atomic weight of zinc.[1] The manipulation of the specimens of oxide and of the gases was also the same as on the former occasion. We stated in our account of the work upon zinc that, in our judgment, the necessary errors connected with the gas analytical part of the determinations could not exceed 1 per cent. of the correction. To test the reasonableness of this estimate, we made determinations of oxygen in 3 specimens of air whose volumes varied between 0.4 and 0.5 cc. The percentages of oxygen found were 20.79, 20.98, and 20.80.

According to C. Langer and V. Meyer[2] nitric oxide is not at all dissociated at temperatures between 900° and 1200°. Emich,[3] on the other hand, states that the dissociation begins at 700°, is small at 900°, is only two-thirds completed at 1200°, and is not finished until the fusing temperature of platinum is reached. The results of both investigations indicate that the temperature of initial dissociation is higher, and its progress slower, than had hitherto been supposed. In view of the fact, therefore, that our oxide was never heated much above 800°, we had to fear the presence in it of oxides of nitrogen, a condition which would have increased very greatly the difficulty of the problem in hand. The following method of testing for the presence of nitric oxide, or other oxides of nitrogen, was adopted: A wide-mouthed salt bottle was moistened on the inside with water; a crucible containing a quantity of cadmium oxide which had been heated to constant weight was introduced; a small quantity of dilute sulphuric acid, free from nitric acid, was added to the oxide and the bottle closed. After standing for several hours, the liquid within was tested for nitric acid by the brucine reaction. None was found. In the subsequent work, the acid in which a specimen of oxide had been dissolved, was examined, in every case, by means of the brucine reaction. In no instance, however, was any evidence of the presence of nitric acid found. In view of the fact that about 20 per cent. of the gas retained by the oxide proved to be free oxygen, we

[1] This JOURNAL, **20**, 196. [2] Pyrochemische Untersuchungen, Seite 66.
[3] Monatschefte für Chemie, **13**, 615.

judged that an examination of the solution, in the manner indicated, was sufficient to demonstrate the presence or absence of nitric oxide or other oxides of nitrogen.

Having converted the dried nitrate into a uniformly dark brown mass, at low temperature, the crucibles were placed in the furnace, previously described, and heated for a period of five or six hours. The tare was then heated for the same length of time, and the weight of the oxide determined. This operation was repeated, without variation, from five to eight times, until no change in the weight of the oxide could be detected after three successive heatings. The crucibles containing the oxide were then brought into our apparatus for dealing with the occluded gases, and there the oxide was treated in the same manner as the oxide of zinc in our earlier work.[1]

When the oxide of zinc is dissolved in dilute sulphuric acid, the evolution of the gas is slow, and continues as long as any of the material remains undissolved. In the case of the oxide of cadmium, on the other hand, a very different phenomenon presents itself. The instant the dilute acid strikes the oxide in the vacuum, there is an almost explosive evolution of gas; and though the solution of the oxide requires some time, but little gas is obtained after the instant of first contact between acid and oxide. The water vapor in the space above the crucibles condenses to a visible mist which settles upon the interior glass surfaces. The disturbance in the oxide, during this sudden liberation of gas, is so great that we were obliged to take measures to prevent it from being thrown out of the crucibles. The gas was collected and analyzed in precisely the same manner as that obtained from the oxide of zinc.

The results of the 9 determinations which were made are presented in the following table:

[1] This JOURNAL, **20**, 195.

	Weight of cadmium.	Weight of oxide.	Uncorrected atomic weight.	Volume of gas (st. cond.). cc.	Percentage of oxygen.	Corrected atomic weight.
1	1.93188	2.20764	112.092	0.574	21.25	112.392
2	1.67935	1.91910	112.074	0.480	25.16	112.365
3	1.48430	1.69620	112.076	0.441	19.95	112.376
4	1.36486	1.55972	112.071	0.402	18.33	112.368
5	1.50295	1.71744	112.112	0.419	21.95	112.394
6	1.43804	1.64330	112.093	0.431	18.56	112.395
7	1.44041	1.64604	112.079	0.406	20.93	112.365
8	1.45938	1.66771	112.082	0.421	21.85	112.375
9	1.40379	1.60420	112.076	0.390	19.50	112.359
			Mean = 112.084			Mean = 112.377

The uncorrected result, 112.084, is very close to the value 112.071 (112.06 with all corrections applied to weighings) which was obtained by Morse and Jones[1]; while the corrected result, 112.377, accords equally well with the mean values 112.39 and 112.38, which were obtained by Bucher[2] in his work upon the chloride and bromide of cadmium.

The relation of the volume of the occluded gas to the weight of the oxide is remarkably constant, as will be seen from the following table, in which is given for the individual determinations the volume of gas per gram of oxide:

	cc.		cc.		cc.
1	0.260	4	0.258	7	0.246
2	0.250	5	0.244	8	0.252
3	0.260	6	0.262	9	0.243

The mean volume of the gas per gram of the oxide is 0.253 cc. as against 0.301 for the oxide of zinc.

A few experiments were made in order to determine whether the gas could be extracted without dissolving the oxide. The first of these was to ascertain whether the oxide, under water, would lose any portion of its gas when left for a long time in a vacuum. The bulb containing the acid was emptied and thoroughly washed with pure water, and then filled with water of perfectly neutral reaction. The water in the bulb was exhausted by occasional pumping until no trace of air could be obtained from it. A specimen of the oxide which had been heated for the usual length of time, was then

[1] This JOURNAL, 14, 264. [2] Dissertation, pages 11–18.

brought into the apparatus and covered with water. After exhausting again as completely as possible, connection with the pump was cut off and the oxide allowed to stand undisturbed for three days in the vacuum. Not a trace of gas was liberated. The next experiment was to determine whether boiling water would liberate the gas. A specimen of the oxide, weighing 1.4134 grams, which had been heated the usual length of time, but not tested as to the constancy of its weight, was heated for six hours under boiling water, and then dissolved in a vacuum. The volume of gas obtained was 0.403 cc., or 0.284 cc. per gram of the oxide. It appears, therefore, that the oxide of cadmium does not lose its gas, either under water in a vacuum or under boiling water at atmospheric pressure.

Two experiments were made to determine whether oxide of cadmium still retains gas when heated to a temperature at which it begins to volatilize. The oxide was reduced to constant weight, and then, by substituting common blast-lamps for those ordinarily used, the temperature of the furnace was raised to a point lying between the fusing temperatures of pure silver (960°) and potassium sulphate (1066°). At this temperature the oxide lost in weight, very slowly but, nevertheless, steadily; and the white porcelain of the crucibles became tarnished with a yellow coating, proving unmistakably that sublimation had begun.

Both samples of the oxide were four times reheated, each time for six hours, and weighed after each heating. The separate losses were very minute; and, altogether, they amounted only to 1 milligram in one case, and to 0.57 milligram in the other, showing that we had not exceeded the temperature of initial volatilization. When these specimens of oxide were afterwards dissolved in a vacuum, one of them gave 0.240 cc. and the other 0.247 cc. of gas per gram of oxide.

The gas from the oxide of cadmium was examined spectroscopically, after removal of the oxygen, and found to be nitrogen.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1898.

Contributions from the Chemical Laboratory of Harvard College.

CVIII.—A TABLE OF ATOMIC WEIGHTS.[1]

By Theodore William Richards.

Since no natural constants are more used by chemists than the atomic weights, it is a matter of great importance for every one, from the chemical philosopher to the practical analyst, to have a convenient table of them always at hand. Unfortunately the present state of our science makes the selection of the values often a matter of personal opinion; and because this is the case, it is well that many of those who have had experience in accurate quantitative analysis should express their views. Hence arose the present work, which was begun solely for use in Harvard College.

It is true that an accurate table of atomic weights may sometimes be less appropriate for the calculation of analyses than an inaccurate one, for the constant errors of any one process are eliminated as much as possible from the accurate table, and, moreover, all the results are reduced to the vacuum standard. Of course neither of these refinements is to be expected in common work, although many uncorrected methods may yield results which are very consistent among themselves. Obviously the best table for the practical calculation of analyses would be a list of factors, in which each quantity had been found empirically according to precisely the method which is to be employed in the analysis of an unknown substance.[2] Since, however, the errors of ordinary work often eliminate one another, and since such a table of empirical factors would have to be accompanied by exceedingly minute directions, the scientifically accurate table of atomic weights is generally the most convenient substitute for the factors demanded by the analyst, as well as the most suitable basis for theoretical considerations concerning the periodic system of the element.

In the compilation of the following table the chief emphasis has been laid on the probable chemical accuracy of the processes involved in each case. The search for possible

[1] Presented to the American Academy of Arts and Sciences, March 9, 1898.

[2] Compare Seubert: Ber. d. chem. Ges., 31, 2180.

causes of constant chemical error has usually furnished the evidence, if any evidence was to be obtained, upon which has been based the sometimes very puzzling decisions between conflicting data. For example, the possible occlusion of foreign matters by many precipitates has always been borne in mind, as well as the fact that crystals obtained from aqueous solutions usually retain with great obstinacy important amounts of mother-liquor enclosed within their structure. Oxides and other substances obtained by ignition often have a tendency to occlude traces of other materials remaining from their mother compound; of course the possibilities of such a serious error must be carefully weighed in each case. Most experimenters upon the volumetric ratio of silver to the chlorides have produced erroneous data, through lack of knowledge of the dangers of this apparently simple process. These results must then be given small weight, no matter how concordant they may seem. The solubility of glass and porcelain, as well as nearly all precipitates, is another frequently overlooked source of grave complications, and so is the action of many substances upon their containing vessels at high temperatures. The fact that in some cases the necessary methods of calculation greatly magnify the experimental error was not forgotten. These and many other equally obvious minor principles have served as the guides in the selection of the figures below; but of course the results cannot be considered ultimate. "Post-mortem examinations are often unable to detect the more subtle poisons." In many cases much more experimental work is needed, not only to secure new data, but also to show where the old are in error. While, however, it is very important to show such falsity, the attempt to counteract it numerically by the application of small corrections, is a dangerous remedy; for minor conditions often seriously modify the minor corrections. In such cases wholly new data must usually be obtained, and these must be corrected, if correction is necessary, by him who is familiar with every step of the processes involved.

One is continually reminded, as he studies the conflicting evidence of the words of Ostwald: "Differenzen sind nicht selten, und mahnen ernstlich an die Unvollkommenheit

menschlicher Arbeit, aber auch an die Verantwortung, welcher jeder übernimmt, welcher einen numerischen Wert der Oeffentlichkeit mitteilt."[1] This responsibility is not always realized by eager investigators, who seek to make up for a possible lack of quality by a superabundance of quantity. "A single determination, well worked out, is better than twenty incomplete ones. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labor for a reviser in the future."[2] Every reaction must be assumed to involve some constant error, and every substance must be assumed to contain some constant impurity, until a proof of the contrary is obtained. Our wofully discordant data furnish a heavy presumption against almost any chemical method, when greater accuracy than one part in four or five hundred is desired.

The standard O = 16.000 is adopted below, as likely to be the most convenient for many years to come.[3] The last figure of each number given in the following table cannot be considered in any case certain. It is often probably not much more than one unit in error, although the uncertainty may amount to as much as six or eight units in some cases. Of course the decimal notation does not admit of closer indications without an individual explanation in each case. For example: iron, germanium, and gallium are given in the table as 56.0, 70.0, and 72.5 respectively. The first is probably known within 0.1 or 0.2, while the other two may easily be 0.5 in error; but the method of expressing the results does not admit of this grade of distinction.

The aim has been to construct a convenient working table, which shall carry with it all that is trustworthy, and nothing that is unnecessary. It is almost needless to state that the well-known standard works of Clarke, Meyer and Seubert, Ostwald, Van der Plaats, and others, have been freely consulted in the preparation of this table, as well as many of the original papers.

[1] Ztschr. phys. Chem., **3**, 143. [2] Proceedings Amer. Acad., **31**, 99; **26**, 294.
[3] Compare F. W. Küster: Ztschr. anorg. Chem., **14**, 251.

Especially am I indebted to Professor Clarke for his latest gigantic collection of data and results,[1] which would have made the present table a work of supererogation, if he had viewed the subject from a somewhat less mathematical standpoint. Professor Clarke's method of decision places the credit with the skilful manipulator; I have striven to give the thoughtful chemist who is not so clever with his hands the credit which I think belongs to him. The fact that the two tables usually agree is due either to the best methods having fallen into the best hands; or to Professor Clarke's having wisely forsaken the rigid application of his principle; or else, especially in the case of the rare metals, to the lack of data affording room for intelligent difference of opinion. Among the seventy-four atomic weights given in the table, only seven differ enough from the values computed by Clarke to excite remark. It seems fitting to give a brief statement of the reasons for the differences in those seven cases, leaving the details of reasoning about the other sixty-seven elements unpublished. The elements mentioned are antimony, cadmium, calcium, magnesium, platinum, tungsten, and uranium.

It is not my purpose to enter at length into the discussion of the antimony problem. Much of the voluminous work upon this subject is now rejected by common consent. The work of Bongartz,[2] sometimes accepted as the best because it is the most recent, has the grave faults inherent in all methods which involve the precipitation of baric sulphate. Among all the published data Cooke's analyses of antimonious bromide[3] (Sb = 119.92) seem to me the most satisfactory, because of the admirable fitness of argentic bromide for quantitative work, and because of the many precautions used in both preparation and analysis. Cooke's[4] and Schneider's[3] work upon the sulphide (Sb = 120.5) are perhaps the next in order; but Cooke's work upon this subject was far less satisfactory than his work on the bromide. Accordingly, the value 120.0 is given as the atomic weight of antimony in the accompanying table, instead of 120.43, computed by Clarke.

[1] Smithson. Misc. Coll., Constants of Nature, **5**, (1897).
[2] Bongartz: Ber. d. chem. Ges., **16**, 1942, (1883).
[3] Cooke: Proc. Am. Acad., **5**, 13, (1877).
[4] Schneider: Pogg. Ann., **98**, 293, (1856); Jour. prakt. Chem. (2), **22**, 131, (1880).

Although the atomic weight of cadmium has been the subject of many investigations, it is still far from certainly established. Many reasons combine to make me think that the highest of the published values are the most accurate. Dumas'[1] work upon the chloride of cadmium led to the value 112.23; but his method of investigating chlorides sometimes gave him too low results.[2] V. Hauer[3] and Partridge[4] found cadmium equal to less than 112 by heating cadmic sulphate in a stream of hydric sulphide, but there is no proof that their initial substance was thoroughly dried. On the other hand, Bucher's conversion of cadmic sulphate into the oxide led to the value 112.36, which Bucher regards as the minimum.[5] This method is one in which the tendency of the oxide to retain sulphuric acid is approximately neutralized by the tendency of the sulphate to retain water; this fact, is demonstrated by Baubigny's[6] good results on zinc, nickel, and aluminium, as well as Marignac's[7] on magnesium. The results of Lenssen,[8] Partridge, Morse and Jones,[9] and Bucher, involving the use of cadmic oxalate, all in the neighborhood of 112, are likely to be too low because of the great difficulty of freeing this substance from water. Morse and Jones have clearly indicated this and other possible causes of error. Moreover, I doubt very much if it is possible to prepare the oxalate free from the nitrate by precipitation from solutions containing cadmic nitrate. The method of calculation magnifies either error by introducing it in opposite directions into the numerator and denominator. Bucher's extended work casts grave doubts upon cadmic oxide (used by Morse and Jones, and Lorimer and Smith)[10] as a suitable substance to serve for a basis of operations. On the other hand, the work of Huntington[11] and

[1] Dumas: Ann. Chem. (Liebig), **113**, 27, (1860).

[2] See Proceedings Am. Acad., **30**, 371. Cases in point: barium, strontium, sodium, and tin.

[3] Von Hauer: Jour. prakt. Chem., **72**, 350, (1857).

[4] Partridge: Am. Jour. Sci. (3), **40**, 377, (1890).

[5] J. E. Bucher: Johns Hopkins Inaug. Dissertation, Baltimore, (1892).

[6] Baubigny: Compt. rend., **97**, 906, 951, 1369, (1883).

[7] Marignac: See under magnesium, later in this paper. Compare Proceedings Am. Acad., **26**, 260, 273; **31**, 160.

[8] Lenssen: Jour. prakt. Chem., **79**, 281, (1860).

[9] Morse and Jones: This JOURNAL, **14**, 260.

[10] Lorimer and Smith: Ztschr. anorg. Chem., **1**, 364.

[11] Proceedings Am. Acad., (1881), p. 28.

Bucher with a bromide (a very satisfactory substance as to its preparation because it may be sublimed, and as to its analysis because of the insolubility of argentic bromide), and that of Bucher with cadmic chloride, point toward 112.3 or 112.4 as the probable figure. The electrolytic work of Hardin[1] upon these compounds, performed unfortunately with small amounts of material, is nevertheless in favor of the lower value, 112.0, so that any value adopted must be uncertain. Clarke computes 111.95; for the following table, 112.3 has been chosen.

There is good reason for believing that Clarke's value for calcium (40.07) is probably too high. The only determinations worth considering are those of Erdmann and Marchand upon the composition of Iceland spar, and only one out of their thirteen experiments is corrected for known causes of constant error.[2] This experiment, which really constitutes the sum and substance of our pseudo-accurate knowledge of a very important quantity, makes calcium almost exactly 40.0. Obviously but little confidence may be placed in such meagre material; it is surprising enough that so common an element has remained forty years untouched on so unsatisfactory a basis. An extended investigation, now well advanced in this laboratory, has as its object the securing of less impeachable data upon the atomic weight of this frequently appearing constituent of the universe.

Marignac's[3] results from the quantitative ignition and synthesis of magnesic sulphate, processes in which the constant errors are likely to eliminate one another, have been so completely confirmed by the recent work of Richards and Parker,[4] that magnesium is represented by the figure 24.36 in the table. The results of the syntheses of magnesic oxide by Burton and Vorce[5] have been shown by Richards and Rogers[6] to be under the cloud of a serious possible constant error, and no other results offer weighty evidence against the value just named.

[1] Hardin: Jour. Am. Chem. Soc., **18**, 1016, (1896).
[2] Erdmann and Marchand: Jour. prakt. Chem., **50**, 237, (1850).
[3] Marignac: Arch. Sci. Phys. et Nat. (3), **10**, 206.
[4] Richards and Parker: Proceedings Am. Acad., **32**, 53; Ztschr. anorg. Chem., **13**, 81, (1896).
[5] Burton and Vorce: This JOURNAL, **12**, 219, (1890).
[6] Richards and Rogers: Proceedings Am. Acad., **28**, 200.

An important deviation from the usually accepted figures is to be seen in the value assigned to platinum below. Our knowledge of the atomic weight of this element depends chiefly upon the elaborate and carefully executed work of Seubert[1] and Halberstadt,[2] and the only question is how this is to be interpreted. These chemists studied the platinchlorides and platinbromides of potassium and the platinchloride of ammonium, weighing these compounds and some of the products of their decomposition. The careful study of the results shows at once that some source of error lies hidden in all the data, for the various ratios are not wholly consistent, even in any one series. Any value from 194.7 to 196.0 may be obtained from the figures,[3] the results of Seubert's work being the least discordant among themselves. Dittmar and M'Arthur[4] explain the discrepancy in the case of potassic platinchloride by assuming that the complex salt contains traces of hydroxyl replacing the halogen and traces of hydrogen replacing the potassium, as well as a small amount of extra occluded potassic chloride. They adduce experimental evidence in proof of this view, but Seubert showed in his reply[5] that their hypotheses can hardly be applied to his determinations. Most of Seubert's and Halberstadt's inconsistencies may be explained by the supposition that the complex salts, like all substances crystallized from aqueous solution, contain certain traces of mother-liquor held in minute cells within the crystal structure, and that these traces of water are not free until the substance is disintegrated. I have accumulated a large amount of experimental evidence, soon to be published, upon this subject. Water is one of the most dangerous, although one of the least heeded, impurities in this kind of work ; and in my opinion it is responsible for the lack of agreement in this case. Hence the best data for the calculation of the atomic weight of platinum seem to be those concerning the relation of the metallic platinum to the potassic chloride or potassic bromide formed by the decomposition of

[1] Seubert : Ber. d. chem. Ges., **14**, 865, (1881).
[2] Halberstadt : *Ibid.*, **17**, 2962, (1884).
[3] Clarke : Recalculation, (1897), p. 334.
[4] Trans. Roy. Soc. Edinburgh, **33**, Part II, 561, (1887).
[5] Ber. d. chem. Ges., **21**, 2179.

the complex salts, for the water must surely have been expelled from these products of the ignition. According to Clarke[1] potassic platinchloride yields 40.101 per cent. of platinum and 30.671 per cent. of potassic chloride,—the means of the closely agreeing results of Seubert and Halberstadt,—while according to Halberstadt potassic platinbromide yields 25.915 per cent. of platinum and 31.591 per cent. of potassic bromide. Disregarding the weight of the complex salt, and assuming that KCl = 74.595, and KBr = 119.095, it is easy to calculate the respective values 195.06 and 195.39 for platinum. The mean of these two values, 195.2, is given below, instead of Clarke's 194.89. The possible occlusion of potassic halide by the complex salt may render even 195.2 too low; but more investigation is evidently needed to prove this.

The same errors may enter into the work on other platinum metals; indeed Seubert[2] admits that traces of water were contained in some of his salts, but he applies no correction for this serious cause of inaccuracy. Since, however, Clarke's method of combining the discordant results seems more nearly to eliminate the error in these cases, his values for these elements are but little changed in the following table.

Feeling wholly unable to decide the present controversy between the two conflicting values (184.9 and 184.0) now proposed for tungsten, I have chosen the mean 184.4 as a compromise which cannot be much more than 0.3 per cent. out of the way.[3]

Uranium, the highest of all the atomic weights, is one of the least satisfactorily determined. Recent investigation upon this subject at Harvard seems to show that all the published data are complicated by constant errors, which, however, sometimes partly eliminate one another; accordingly the round number 240, instead of Clarke's 239.59, is printed in the table. The discussion is better deferred until our work has taken more definite shape.

Besides these seven elements, there are seventeen more whose atomic weights, as given in the following table, differ from the results of Professor Clarke's computations by one

[1] Recalculation, page 333. [2] Ann. Chem. (Liebig), **261**, 262.
[3] Compare Hardin: J. Am. Chem. Soc., **19**, 657, (1897).

part in a thousand or more. As none of the seventeen values is known certainly to within one part in five hundred, and some of them are probably at least as much as one per cent. in error, differences in these cases will excite no especial remark. The elements are: cerium, columbium, erbium, gadolinium, gallium, glucinum, indium, lanthanum, neodymium,[1] osmium, palladium, praseodymium, samarium, scandium, thorium, ytterbium, and zirconium. This is by no means a complete list of the uncertain elements, but only of those for which the data admit of slightly different interpretations.

It is rather unfortunate that most classified tables of the elements omit the fractional parts of the atomic weights, for these fractions will undoubtedly play an essential part in the ultimate solution of the de-Chancourtois-Newlands-Mendeléeff-Meyer mystery. In order to present a modern table which will supply these omissions, as well as afford at a glance an approximate idea of the probable error in each case, I have repeated the values in the natural order. From the classified table have been omitted several elements whose atomic weights and properties are uncertain; their presence in the system serves rather to obscure well-known relations than to elucidate new ones. That this procedure is an omission of incompleteness is evident; the last part of the table is at best a lame affair. The form proposed by Thomsen[2] is perhaps the most generally satisfactory of the current modes of arrangements, but his last row is unwieldy both for printing and for thinking. In the accompanying table a compromise has been adopted which cannot fail to be comprehensible; it is not my purpose here to enter into the arguments regarding the adequacy of the various forms.

This table will be reprinted, with any changes which may

[1] Since the publication of this paper in the Proceedings of the American Academy, H. C. Jones has published a research upon the "dymia" which far exceeds in accuracy and completeness the vague statements of their first separator. Oddly enough the new values are the old ones interchanged. While it is impossible to say how nearly the new figures represent the peculiarly elusive values in question, they carry with them much greater weight than the old ones, and are given, as far as the first decimal place, in the following table. See this volume, p. 345. The value 142 for the mixture "didymium" is also given for convenience in the calculation of analyses in which it is not possible to separate the twins.

[2] Ztschr. anorg. Chem., 9, 190.

be necessary, every year. Since the commencement of the work I have been glad to hear of the appointment of a committee by the German Chemical Society to accomplish a similar purpose, the American Chemical Society having for several years possessed such a committee. The matter cannot receive too much intelligent examination.

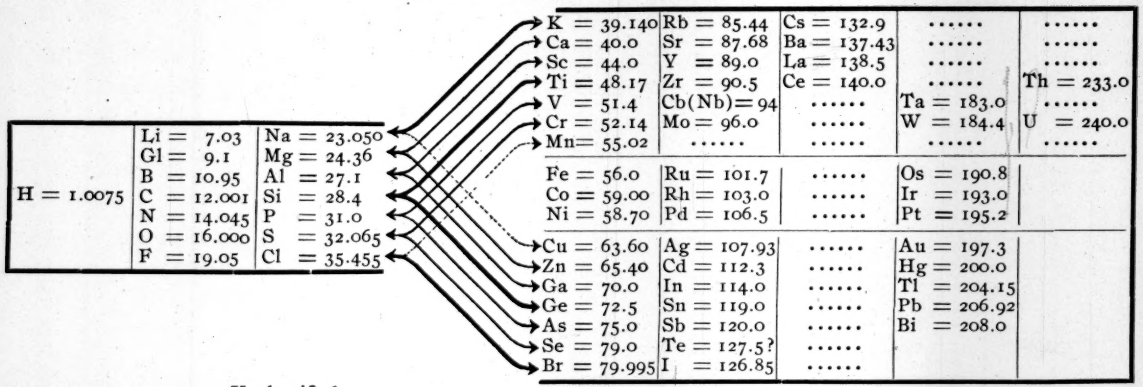
A TABLE OF ATOMIC WEIGHTS

OF SEVENTY-FOUR ELEMENTS.

Compiled in March, 1898, from the Most Recent Data.

Name.	Symbol.	Atomic weight.
Aluminium	Al	27.1
Antimony	Sb	120.0
Argon	A	39.9?
Arsenic	As	75.0
Barium	Ba	137.43
Beryllium	Be = Gl	9.1
Bismuth	Bi	208.0
Boron	B	10.95
Bromine	Br	79.955
Cadmium	Cd	112.3
Caesium	Cs	132.9
Calcium	Ca	40.0
Carbon	C	12.001
Cerium	Ce	140.0
Chlorine	Cl	35.455
Chromium	Cr	52.14
Cobalt	Co	59.00
Columbium	Cb = Nb	94.0
Copper	Cu	63.60
"Didymium"	Nd + Pr	142 ±
Erbium	Er	166.0
Fluorine	F	19.05
Gadolinium	Gd	156.0?
Gallium	Ga	70.0
Germanium	Ge	72.5
Glucinum	Gl = Be	9.1
Gold	Au	197.3
Helium	He	4.0?
Hydrogen	H	1.0075
Indium	In	114.0
Iodine	I	126.85
Iridium	Ir	193.0
Iron	Fe	56.0
Lanthanum	La	138.5

Name.	Symbol.	Atomic weight.
Lead	Pb	206.92
Lithium	Li	7.03
Magnesium	Mg	24.36
Manganese	Mn	55.02
Mercury	Hg	200.0
Molybdenum	Mo	96.0
Neodymium	Nd	143.6
Nickel	Ni	58.70
Niobium	Nb = Cb	94.0
Nitrogen	N	14.045
Osmium	Os	190.8
Oxygen (standard)	O	16.000
Palladium	Pd	106.5
Phosphorus	P	31.0
Platinum	Pt	195.2
Potassium	K	39.140
Praseodymium	Pr	140.5
Rhodium	Rh	103.0
Rubidium	Rb	85.44
Ruthenium	Ru	101.7
Samarium	Sm	150.0
Scandium	Sc	44.0
Selenium	Se	79.0
Silicon	Si	28.4
Silver	Ag	107.93
Sodium	Na	23.050
Strontium	Sr	87.68
Sulphur	S	32.065
Tantalum	Ta	183.0
Tellurium	Te	127.5
Terbium	Tb	160.0
Thallium	Tl	204.15
Thorium	Th	233.0
Thulium	Tu	170.0 ?
Tin	Sn	119.0
Titanium	Ti	48.17
Tungsten	W	184.4
Uranium	U	240.0
Vanadium	V	51.4
Ytterbium	Yb	173.0
Yttrium	Yt	89.0
Zinc	Zn	65.40
Zirconium	Zr	90.5



			K = 39.140	Rb = 85.44	Cs = 132.9	.....	.....
			Ca = 40.0	Sr = 87.68	Ba = 137.43	.....	.....
			Sc = 44.0	Y = 89.0	La = 138.5	.....	.....
			Ti = 48.17	Zr = 90.5	Ce = 140.0	.....	Th = 233.0
			V = 51.4	Cb(Nb) = 94	.....	Ta = 183.0	.....
			Cr = 52.14	Mo = 96.0	.....	W = 184.4	U = 240.0
			Mn = 55.02	.....	.....	.....	.....
			Fe = 56.0	Ru = 101.7	.....	Os = 190.8	
			Co = 59.00	Rh = 103.0	.....	Ir = 193.0	
			Ni = 58.70	Pd = 106.5	.....	Pt = 195.2	
			Cu = 63.60	Ag = 107.93	.....	Au = 197.3	
			Zn = 65.40	Cd = 112.3	.....	Hg = 200.0	
			Ga = 70.0	In = 114.0	.....	Tl = 204.15	
			Ge = 72.5	Sn = 119.0	.....	Pb = 206.92	
			As = 75.0	Sb = 120.0	.....	Bi = 208.0	
			Se = 79.0	Te = 127.5?	.....		
			Br = 79.995	I = 126.85	.....		
H = 1.0075	Li = 7.03	Na = 23.050					
	Gl = 9.1	Mg = 24.36					
	B = 10.95	Al = 27.1					
	C = 12.001	Si = 28.4					
	N = 14.045	P = 31.0					
	O = 16.000	S = 32.065					
	F = 19.05	Cl = 35.455					

Unclassified :

Helium	= 2.0 or 4.0 ?	Gadolinium	= 156.0
Argon	= 19.94 or 39.9 ?	Terbium	= 160.0
Praseodymium	= 140.5	Erbium	= 166.0
Neodymium	= 143.6	Thulium	= 170.0
Samarium	= 150.0	Ytterbium	= 173.0

Anomalous :

Cobalt	= 59.00
Nickel	= 58.70
Tellurium	= 127.5

Contributions from the Sheffield Laboratory of Yale University.

LXI. — RESEARCHES ON THE CYCLO AMIDES: α-KETOBENZMORPHOLINE AND α-BENZ-PARAOXAZINE DERIVATIVES.

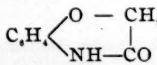
By H. L. Wheeler and Bayard Barnes.

α-Ketobenzmorpholine, or from its method of preparation called orthoaminophenoxyacetic acid anhydride, has the structure of a cyclo amide and should act like an acid amide or, in other words, as if it were a derivative of the two forms, $\overset{\lceil\text{———}\rceil}{\text{NH}-\text{CO}}$ and $\overset{\lceil\text{———}\rceil}{\text{N}=\text{COH}}$. The literature on this compound would seem to indicate that it is a very inactive substance, since no derivatives of it have hitherto been prepared. It will be shown, however, in this paper, that this compound behaves like an amide and yields derivatives which, in their properties, are closely related to the corresponding compounds of formanilide.

Orthoaminophenoxyacetic anhydride was first obtained by Fritzsche[1] by reducing orthonitrophenoxyacetic acid with stannous chloride. According to Thate,[2] this compound is not obtained pure by Fritzsche's method, but is best prepared by reducing the nitro compound with iron and acetic acid.

Aschan[3] obtained this so-called anhydride from orthoaminophenol and chloracetyl chloride. He states that concentrated acids and alkalies have no effect on the substance, but that it reacts energetically with phosphorus pentachloride, with at least partial decomposition.

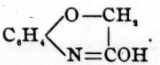
The latest work on the subject is that of Duparc.[4] At Gräbe's suggestion he undertook the examination of this anhydride in order to determine which of the following formulas is to be assigned to the substance:



(α-Ketobenzmorpholine.)

I.

or



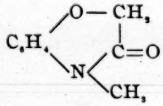
(α-Oxybenzparaoxazine.)

II.

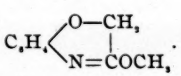
[1] J. prakt. Chem. [2], **20**, 288.
[2] *Ibid.* [2], **29**, 180.
[3] Ber. d. Chem. Ges., **20**, 1523.
[4] *Ibid.*, **20**, 1943.

Duparc found that the material was not acted on by acetic anhydride even at 180°, and since he did not succeed in obtaining a reaction with methyl iodide or nitrous acid he abandoned the subject.

We have taken up the work at this point and find that a sodium and silver salt of this cyclo amide can easily be prepared, and that the action of alkyl iodides on these salts give two series of isomeric alkyl compounds. Those obtained from the sodium salt have the alkyl group joined to nitrogen and are to be considered as α-ketobenzmorpholine derivatives, Formula III., while those from the silver compound have the alkyl group attached to oxygen, and are cycloimidoesters or benzparaoxazine[1] derivatives, Formula IV.



III.



IV.

The structure of these compounds is settled from the following: The product obtained by the action of methyl iodide on the sodium salt gave on prolonged heating with concentrated hydrochloric acid, at a high temperature, orthomethylaminophenol, $C_6H_4\begin{cases}OH\\NHCH_3\end{cases}$, thus showing, in the case of the sodium salts, that the alkyl groups attach themselves to nitrogen.

On the other hand, the products obtained from the silver salt, even on treating with cold dilute hydrochloric acid, immediately regenerate α-ketobenzmorpholine. This instability in the presence of acids, being a characteristic property of substituted imido esters, shows that in this case the alkyl groups are attached to oxygen.

[1] Hitherto only two benzparaoxazine derivatives have been prepared. The compound obtained by reducing orthonitrophenylacyl ether, *i.e.*, $C_6H_4\begin{cases}O-CH_2\\|\\N=C.C_6H_5\end{cases}$, and the analogous methyl derivative, are sometimes called β-phenyl and β-methylbenzparoxazines (Ber. d. chem. Ges., **23**, 172). From analogy with the quinoline derivatives, quinaldine, for example, being called α-methylquinoline, these compounds should be termed α- and not β-derivatives. The latter nomenclature is used in this paper.

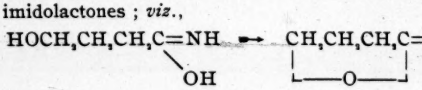
It will be noticed that the above behavior of the sodium and silver salts of α-ketobenzmorpholine is perfectly analogous to that of the salts of the anilides. Indeed the analogy by no means ends in this behavior but extends also to the derivatives. The cycloimido esters obtained from the silver salt of α-ketobenzmorpholine have strong, peculiar odors, and decompose into ketobenzmorpholine on exposure to the air; the isomeric compounds have no odor and are stable on exposure. The compounds from the silver salt behave precisely like the isoanilides or substituted imido esters, not only in being immediately decomposed by acids but also inasmuch as they react with bases, at ordinary temperature, giving amidines. These amidines, some of them difficult to crystallize, give well-crystallized salts.

Again, the silver salt of α-ketobenzmorpholine reacts with acyl chlorides, like the silver salts of the anilides, giving well-crystallized acyl derivatives. These derivatives have the acyl group attached to nitrogen. It is noteworthy that, in spite of the failure of Duparc to obtain an acetyl derivative by means of the keto compound and acetic anhydride, such a compound results, with evolution of heat, from the silver salt. Moreover, this acetyl compound is so stable that it can be crystallized from water without decomposition.

It is now shown that α-ketobenzmorpholine behaves precisely like formanilide, and therefore the normal structure is to be assigned to this cyclo amide, *i. e.*, Formula I.

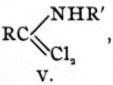
That the amides in general are derivatives of the structure $-NH-\overset{|}{C}O$ and not $-N=\overset{|}{C}OH$, or, in other words, that they have the keto and not the enol form follows from the behavior of their oxy compounds.

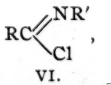
It is well known that the oxy acids, especially the gamma and delta derivatives, readily separate water, giving lactones. If the amides had the second of the above structures they would be imido acids and their oxy compounds would be expected to separate water, like the oxy acids themselves, giving imidolactones; *viz.*,

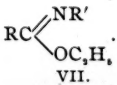


Imidolactones have not yet been obtained. The oxyamides do not form anhydrides in this manner. For example: gamma-oxyvaleramide results by heating gamma-oxyvalerianic anhydride or the ester with ammonia to 100°. On boiling this oxyamide it slowly decomposes, giving off ammonia and not water; indeed some of these oxyamides boil unaltered. These facts not only show that the acid amides have the normal structure, but they also dispose of the theory that in these compounds the enol and keto form exist in a state of equilibrium.

Lachmann[1] in his interesting paper on the constitution of the acid amides concludes that acetamide and benzamide have hydroxyl groups because they *immediately* give off hydrogen chloride with phosphorus pentachloride. Oxamethane does not immediately decompose in this manner but gives an amide chloride.[2] He, therefore, concludes that oxamethane has a keto group, and that these results point to a division of the amides into two groups, etc. The following considerations show, however, that this is not the true explanation of the behavior of these amides with phosphorus pentachloride. We know from the work of Wallach,[3] Lengfeld and Stieglitz,[4] and others, that the grouping V. (below) is very unstable, the grouping VI. being more stable. It has been shown in papers from this laboratory that the more negative the character of the molecule in this or the analogous grouping VII., the less stable are the compounds. What applies to grouping VII would therefore apply in greater force to grouping V.


V.


VI.

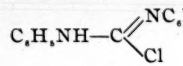

VII.

We now have the true explanation of Lachmann's results. The amide chlorides of acetamide and benzamide are far more negative than the amide chloride of carbonic acid or its ester-amide oxamethane, and, as would be expected, they decompose more easily. The different behavior of the amides with

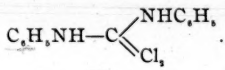
[1] This JOURNAL, 18, 600.
[2] *Ibid.*, 184, 1; 214, 193.
[3] Wallach: Ann. Chem. (Liebig), 184, 1.
[4] This JOURNAL, 17, 99.

phosphorus pentachloride, therefore, does not depend on a difference of structure but on the properties of the amide chlorides.

If this view is correct, it must follow that if we increase the positive character of the molecule VI. by replacing radical R by an imido or anilido group, for example, we should obtain a compound capable of forming a comparatively stable amide chloride corresponding to formula V. This is precisely what takes place. Lengfeld and Stieglitz,[1] in their interesting work on the imidoethers of carbonic acid, have shown that carbodiphenylimide, $C_6H_5N=C=NC_6H_5$, not only unites with 1 molecule of hydrogen chloride, as stated by Weith, giving an imide chloride, formula VIII., but that this compound combines further with hydrogen chloride, and, as would be expected, a stable amide chloride results, which they call carbodiphenylimide dichloride, Formula IX.



VIII.



IX.

Lengfeld and Stieglitz state that this amide chloride melts at 130° and "is quite stable when kept from moisture and organic matter."

From the above it is evident that the results obtained by the action of phosphorus pentachloride on acet- and benzamides do not lead to the conclusion that these compounds have a hydroxyl group. Indeed, it is very improbable that the grouping $-N=\overset{|}{C}OH$ exists in any stable amide whatever.

Experimental Part.

α-Ketobenzmorpholine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ NH-CO\end{cases}$.—This was prepared essentially according to Thate's method.[2] His directions for the purification of both orthonitrophenyloxyacetic acid and the anhydride, obtained by reduction, not being

[1] This JOURNAL, 17, 108. [2] J. prakt. Chem. [2], 29, 148.

suitable for the preparation of the material in large quantities, it was found better to proceed as follows:

After warming the mixture of orthonitrophenol, chloracetic acid and alkali, and filtering, hydrochloric acid was added, and the precipitate distilled in steam to remove unaltered orthonitrophenol. The aqueous solution remaining deposits the orthonitrophenyloxyacetic acid on cooling. For the reduction the acid was suspended in about 20 per cent. acetic acid and iron filings slowly added. After the reduction, the residue was boiled with alcohol and animal charcoal and the anhydride crystallized from alcohol. The melting-point of the material thus obtained is 169°, instead of 166° as given by Thate. It may be crystallized conveniently from alcohol or chloroform. In the latter solvent it is less soluble.

α-Sodiumoxybenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad |\\ N=CONa\end{cases}$. — 0.8 gram of sodium was dissolved in methyl alcohol and 5.0 grams of *α*-ketobenzmorpholine were added. The solution was then evaporated in a vacuum and the residue heated at 100° for several hours, the pressure being kept at about 13 mm. The perfectly dry mass then, on shaking, became granular, and a sodium determination as carbonate gave:

	Calculated for $C_8H_7NO_3.CH_2.ONa$.	Calculated for $C_8H_4NO_3Na$.	Found.
Na	11.33	13.45	13.41

The material thus obtained did not dissolve in water, but *α*-ketobenzmorpholine separated; on adding an excess of alkali this readily dissolved. An attempt to prepare this sodium salt by dissolving the keto compound in alcohol, adding the calculated quantity of sodium ethylate, and then ether, gave no precipitate.

n-Methyl-α-ketobenzmorpholine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad |\\ N-C=O\\ \quad\quad\quad |\\ \quad\quad\quad CH_2\end{cases}$. — This compound was prepared by heating the dry sodium salt of *α*-ketobenzmorpholine, suspended in benzene, to 135° for several hours. It was found, however, that it is unnecessary

to prepare the dry salt as given above. It was more conveniently prepared as follows: 1.6 grams of sodium were dissolved in a small amount of methyl alcohol, 10 grams of α-ketobenzmorpholine were added, and then 20 grams of methyl iodide; the whole was then heated to 135° for about seven hours. The contents of the tube were then filtered from sodium iodide, washed with ether, and distilled at 14 mm. pressure. After the alcohol and ether had evaporated, the material practically all boiled over at 156°. It readily solidified, and, on crystallizing from alcohol, large, stout, colorless prisms were obtained. These melted from 58°–59°, and a nitrogen determination gave:

	Calculated for $C_9H_9NO_3$.	Found.
N	8.58	8.58

It was found that this compound, like the following ethyl derivative, has little or no basic properties. It is insoluble in cold dilute hydrochloric acid. On warming, solution takes place, but, on cooling, the unaltered material separates in the form of needles or prisms. It dissolves more readily in concentrated hydrochloric acid, and is precipitated by water. Platinum chloride gave no precipitate when added to these solutions. A solution of the material in benzene gave no precipitate with dry hydrogen chloride. It is insoluble in alkali.

Orthomethylaminophenol, $C_6H_4\begin{cases}OH\\NHCH_3\end{cases}$. — Not quite 2 grams of the above methyl derivative were heated with concentrated hydrochloric acid to 150°–160° for a number of hours. The hydrochloric acid was then evaporated on the water-bath and the residue treated with water, when it was found that the greater portion of the material had remained unaltered in this treatment; the aqueous filtrate was treated with an excess of sodium carbonate, some sulphurous acid was added, and the whole shaken with ether. On evaporating the ether solution a small amount of almost colorless material separated in the form of plates. This was crystallized from petroleum ether when colorless thin spangles separated. On heating the pure material thus obtained, it began to darken

in color, rapidly at 80°, and decomposed, melting and turning black between 80° and 90°. Seidel,[1] who first obtained this compound, states that it crystallizes in plates that soon oxidize and take on a dark brown color. He says that, on heating, the material darkens and then melts above 80° with decomposition. The properties of the compound obtained by us agree perfectly with this description. We may add, as a further means of identifying this compound, that the hydrochloric acid solution gives a deep red-brown color with ferric chloride.

n-Ethyl-α-ketobenzmorpholine, $C_6H_4<\begin{matrix}OCH_2\\|\\CO\cdot\end{matrix}>N-C_2H_5$.—This was prepared by means of sodium ethylate and ethyl iodide in the same manner as the above methyl derivative. The contents of the tube after the evaporation of the excess of ethyl iodide and alcohol all boiled over from 157°–159° at 15 mm. pressure. This material, unlike the methyl compound, was not obtained in the solid state. It had a light yellow color and a nitrogen determination gave :

	Calculated for $C_{10}H_{11}NO_3$.	Found.
N	7.91	8.20

This compound, like the corresponding methyl derivative, is not affected by acids or alkali under ordinary conditions. It dissolves in concentrated hydrochloric acid and is precipitated again by water. A slight warming is noticed on dissolving the material in concentrated sulphuric acid.

α-Silveroxybenzparaoxazine, $C_6H_4<\begin{matrix}O-CH_2\\|\\N=COAg\end{matrix}$.—This was prepared by dissolving α-ketobenzmorpholine in alcohol and adding, first sodium ethylate (1 molecule) and then the calculated quantity of silver nitrate. The mixture, largely diluted with water, gave a white precipitate which, on stirring, became a light gray powder. This was filtered, washed with water, alcohol, and ether, and dried at a temperature

[1] J. prakt. Chem., **42**, 453.

somewhat below 100°. A silver determination gave the following:

	Calculated for $C_9H_4NO_2Ag$.	Found.
Ag	42.18	42.37

This salt is quite stable in respect to light. It is not readily decomposed by water or alcohol, although phenol immediately reduces it. The behavior of the silver salts of this compound and formanilide with phenols, is peculiar. Silver formanilide and silver 2-4-dichlorformanilide react with phenol with evolution of heat, the salts immediately blackening and regenerating unaltered formyl compound and silver. This is all the more remarkable, since silver 2-4-dichlorformanilide may stand mixed with water or alcohol for days without decomposition. Indeed, it can be boiled with water without any decomposition. Cold glycerin does not affect it, but phenol, largely diluted with benzene, an aqueous solution of hydroquinone, or an alcoholic solution of β-naphthol, almost immediately reduces the salt. A solution of thymol in benzene produces a mirror of silver, and resorcin in water slowly blackens the compound. From the above it is evident that these reactions involve an addition; the addition-products being unstable then decompose into simpler molecules.

α-Methoxybenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad\vert\\ N=COCH_3\end{cases}$.—20 grams of α-silver oxybenzparaoxazine and 20 grams of methyl iodide (1.5 molecules) were heated to 115°–120° for eight hours, the reaction then being practically complete. The material was then taken up in ether and filtered from the silver iodide.[1] The ether solution on evaporation in a vacuum over potash gave an oil which refused to solidify in a freezing-mixture. It was found to boil almost entirely between 135°–136° at 21 mm. pressure. The material thus obtained was a colorless oil with a pleasant odor, perhaps suggesting orange peel. A nitrogen determination gave:

[1] It is advisable to shake the ether solution with alkali in order to remove unaltered orthoaminophenoxyacetic acid anhydride, which always accompanies the reaction product. Compare a-isoamyloxybenzparaoxazine.

	Calculated for $C_9H_9O_2N$.	Found.
N	8.58	8.66

On treating this oil with a drop of dilute hydrochloric acid it immediately solidified, giving crystals of α-ketobenzmorpholine. On exposure to air it slowly absorbs moisture, giving the same result. It is unaffected by cold alkali.

α-Ethoxybenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ N=COC_2H_5\end{cases}$.—23 grams of the above silver salt were heated with ethyl iodide (2 molecules) to 100°–130° for twenty hours. On extracting with ether and evaporating, an oil was obtained which deposited some unaltered α-ketobenzmorpholine. On distilling in a vacuum the oil boiled mostly between 135°–136° at 16 mm. pressure. It had a similar pleasant odor to that of the methoxy compound. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}O_2N$.	Found.
N	7.90	7.68

With acids this compound is immediately decomposed like the methoxy compound. It is unaffected by cold alkali.

α-Isopropyloxybenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ N-COC_3H_7\end{cases}$. — 25 grams of the silver salt and 22 grams of isopropyl iodide were heated for nine hours at 120°–130°. On extracting them with ether, shaking the ether solution with dilute potassium hydroxide, and evaporating, an oil was obtained. This was distilled at 14 mm. pressure, when the greater portion boiled from 137°–138°. The material was colorless and had a peculiar odor, which, unlike the methyl and ethyl derivatives, was not pleasant. A nitrogen determination gave:

	Calculated for $C_{11}H_{13}O_2N$.	Found.
N	7.32	7.31

It decomposes on standing, or with acids, giving α-ketobenzmorpholine.

α-Isobutyloxybenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ N=COC_4H_9\end{cases}$.—25 grams

of the silver salt and 26 grams of isobutyliodide were heated for twenty-two hours at 120°–140°. The reaction-product, treated as above, gave an oil which was distilled at 21 mm. pressure, when it was found to boil practically from 160°–164°. It had a strong, somewhat disagreeable, odor. A nitrogen determination gave:

	Calculated for $C_{12}H_{15}O_2N$.	Found.
N	6.82	6.83

α-Isoamylbenzparaoxazine, $C_6H_4\langle \begin{matrix} O-CH_2 \\ | \\ N=C-OC_5H_{11} \end{matrix}$. — 25 grams of the silver salt and 28 grams of isoamyl iodide were heated to 130°–150° for eighteen hours. On extracting with ether, an oil was obtained which gave no constant boiling-point, the solid anhydride distilling over with the oil. The distillate was taken up in ether and shaken with dilute potassium hydrate; the ether was evaporated and the oil then distilled at 174°–175° at 21 mm. pressure. It was colorless and had a disagreeable odor, somewhat resembling isoamyl oxalate. A nitrogen determination gave:

	Calculated for $C_{13}H_{17}O_2N$.	Found.
N	6.39	6.55

n-Acetyl-α-ketobenzmorpholine, $C_6H_4\langle \begin{matrix} OCH_2 \\ >CO \\ N.COCH_3 \end{matrix}$. — Acetyl chloride reacts violently with dry α-silver oxybenzparaoxazine. For the preparation of this compound six grams of the silver salt were suspended in dry ether and the calculated amount of acetyl chloride was added. On filtering and evaporating, beautiful, long, white needles separated; these melted at 77°. A nitrogen determination gave:

	Calculated for $C_{10}H_9O_3N$.	Found.
N	7.32	7.43

This acyl compound is quite stable. It can be crystallized unaltered from water.

n-Benzoyl-α-ketobenzmorpholine, $C_6H_4\langle \begin{matrix} O-CH_2 \\ >CO \\ N-COC_6H_5 \end{matrix}$. —

Six grams of the silver salt were suspended in benzene and benzoyl chloride added. From the benzene solution beautiful, colorless, compact prisms separated. These melted at 93°, and a nitrogen determination gave :

	Calculated for $C_{16}H_{11}O_2N$.	Found.
N	5.53	5.46

This compound can be crystallized from water.

α-Phenylaminobenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad|\\ N=C-NHC_6H_5\end{cases}$.—When *α*-ethoxybenzparaoxazine and aniline were mixed, in molecular proportions, the mixture solidified after standing twenty-four hours to a white, crystalline mass. It is readily soluble in alcohol from which it crystallizes in colorless, compact prisms melting at 126°. A nitrogen determination was made with the following result :

	Calculated for $C_{14}H_{12}N_2O$.	Found.
N	12.50	12.53

The *hydrochloride* prepared by dissolving the above cycloamidine in aqueous hydrogen chloride separated in the form of colorless, four-sided prisms, which melt with decomposition from 220°–223°.

The *hydroiodide*, $C_{14}H_{12}N_2O.HI$, crystallizes from water in colorless plates, which melt from 195°–196°. An iodine determination gave :

	Calculated for $C_{14}H_{13}N_2OI$.	Found.
I	36.26	35.77

The *nitrate* separates from dilute nitric acid in the form of colorless four- and eight-sided plates, melting at 147°.

α-Metachlorphenylaminobenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad|\\ N=C-NC_6H_4Cl\end{cases}$.—A mixture of *α*-ethoxybenzparaoxazine and 1 molecular preparation of metachloraniline did not solidify after standing a week. The material was then taken up in dilute hydrochloric acid, and, after filtering, the amidine was precipitated with ammonia. It was then ob-

tained in the solid condition and, on crystallizing from benzene, it separated in the form of colorless plates and melted at 112°–114°.

	Calculated for $C_{14}H_{11}N_2O.Cl.$	Found.
N	10.83	10.06

The *hydrochloride*, $C_{14}H_{10}N_2OCl.HCl$, crystallized from alcohol, melts with decomposition at 205°–207°.

α,β-Naphthylaminobenzparaoxazine,

$C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ N=C-NHC_{10}H_7\end{cases}$. — 2.4 grams of *α*-isopropyl benzparaoxazine and 2 grams of *β*-naphthylamine were heated in alcohol for eighteen hours on the steam-bath. On evaporating off the alcohol and crystallizing the residue from benzene, white leaflets separated which melted from 154°–155°.

	Calculated for $C_{18}H_{14}N_2O.$	Found.
N	10.22	10.00

α-Isobutylaminobenzparaoxazine,

$C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ N=C-NHC_4H_9\end{cases}$. — This was obtained by mixing *α*-ethoxybenzparaoxazine with isobutylamine. It forms a thick varnish at ordinary temperature, which, only after long standing, showed evidence of crystallization.

The *hydrochloride* may be crystallized from water or chloroform. From the latter it separates in the form of flakes, melting from 220°–223°.

	Calculated for $C_{18}H_{17}N_2OCl.$	Found.
Cl	14.76	14.40

α-Allylaminobenzparaoxazine, $C_6H_4\begin{cases}O-CH_2\\ \quad\quad|\\ N=C-NHC_3H_5\end{cases}$.— The mixture in this case did not solidify on long standing. It was taken up in benzene and the hydrochloride precipitated by means of dry hydrogen chloride. This precipitate was crystallized from benzene containing some alcohol, when colorless needles, melting at 190°, were obtained. These

were dissolved in alcohol. From the solution ammonia precipitated an oil which soon solidified. This was crystallized from ligroïn with a little benzene, when the material separated in colorless prisms melting at 63°.

The *hydrochloride* is readily soluble in water and alcohol; it was analyzed with the following result:

	Calculated for $C_{11}H_{13}N_2OCl$.	Found.
Cl	15.8	15.9

NEW HAVEN, May, 1898.

LXII.—THE ACTION OF AMINES ON ACYLIMIDO-ESTERS: ACYL AMIDINES.

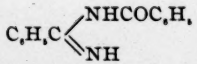
BY H. L. WHEELER AND P. T. WALDEN.

In a previous paper we described a series of acylimido-esters, and stated that they react with ammonia and bases giving acylamidines. We are now prepared to describe some of these amidines and to discuss their formation.

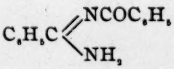
Few acylamidines have hitherto been described. The action of acyl chlorides and anhydrides on the free amidines does not always lead to the formation of acyl derivatives.[1] Pinner obtained benzoylbenzamidine from benzamidine and benzoic acid anhydride, and also from benzonitrile by condensation with sulphuric acid. On account of the ease with which this compound separates ammonia, giving dibenzamide, he assigned the structure represented by Formula I. to this substance.

We have found that the benzoylbenzimido esters, *i. e.*, $C_6H_5C\langle^{NCOC_6H_5}_{OR}$ react with ammonia, giving a compound in every respect identical with that obtained from benzonitrile by the method of Pinner, while an isomeric compound, Formula II., would be expected, if the reaction takes place, as is usually assumed, by double decomposition, replacement or substitution.

[1] Pinner: Die Imidoäther und ihre Derivate.

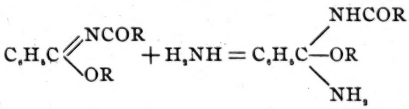


I.



II.

The action of amines on the acylimido esters, like the action of amines on the amidines themselves, does not take place by direct replacement, but involves the intermediate formation of an unstable addition-product :

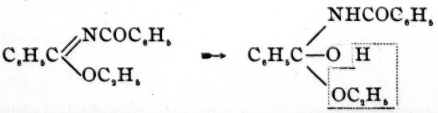


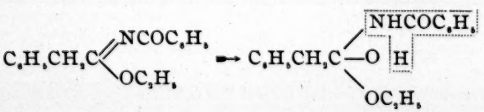
III.

This hypothetical addition-product can then separate alcohol in two ways, giving an acyl amidine corresponding to either of the above forms.

It cannot be maintained that, because benzoylbenzamidine easily decomposes into dibenzamide and ammonia, its structure is to be represented by Formula I., since in this decomposition hydrolysis takes place with addition of water, forming a product similar to III., and the same addition-product must result from I. and II.

That this view is correct and that this decomposition has no significance in regard to the structure of the acyl amidines, is shown by the behavior of the analogously constituted acylimido esters, *i. e.*, benzoylbenzimidoethyl ester and benzoylphenylacetimidoethyl ester. These compounds easily decompose with water, under the same conditions as benzoylbenzamidine, as follows :





That is, the first gives dibenzamide and alcohol, while the second gives benzamide and ethylphenyl acetate. In other words, the first apparently decomposes at a single bond; the second at the double bond. Here are then two compounds, not only of the same structure, but also similar to the acyl amidines, which decompose or are hydrolyzed in two different ways.

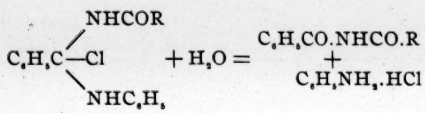
The structure of these amidines cannot therefore be determined by their decomposition-products, and further work will be required before this question is settled.

Beckmann and Sandal,[1] in their interesting work on the rearrangement of α-benzilmonoxime, have recently obtained benzoylbenzimidechloride, $C_6H_5C\begin{matrix}\diagup\!\!=\!\!\diagdown NCOC_6H_5\\ \diagdown\quad\diagup Cl\end{matrix}$, a compound which shows, as would be expected, many properties in common with the acylimido esters. It readily decomposes into dibenzamide and unites with primary bases giving acyl amidines. With ammonia it gives the acyl amidine described by Pinner and with aniline an acyl amidine identical with that obtained by us from the benzoylbenzimido esters. Beckmann and Sandal, however, did not succeed in preparing acyl amidines from this compound and secondary amines, and here it may be stated that we have repeatedly made attempts to prepare acyl amidines from secondary bases and various acylimido esters, but in each case also without success.

In support of Pinner's formula for benzoylbenzamidine, Beckmann and Sandal state that benzaldehyde does not combine with this substance, and that with benzenesulphochloride it gives a compound insoluble in alkali.

The acyl amidines, described below, are stable towards cold alkali. Some of them dissolve in acids and may be precipitated unaltered by alkali or ammonia. They combine with one equivalent of hydrogen chloride to form salts which are comparatively unstable. In aqueous solution these salts soon decompose as follows:

[1] Ann. Chem. (Liebig), **296**, 279.



The diacylamide generally separates pure and in the form of a glistening mass of colorless crystals.

Experimental Part.

Benzoylbenzamidine.—This was formed when 10 grams of benzoylbenzimidonormalpropyl ester were warmed in alcoholic solution with the addition of aqueous ammonia in excess. On diluting the alcoholic solution, in which it is readily soluble, this compound separated as an oil which readily solidifies. It was purified by dissolving or crystallizing it from a mixture of ligroïn and alcohol. It melted constantly at 100°. Pinner[1] gives the melting-point of this compound as 106°. Gumpert[2] states that it melts at 105.5°, and Beckmann and Sandal give 98° as its melting-point. In addition to the above we have prepared this compound from benzoylbenzimidoethyl ester and ammonia. This product also melted at 100°. A nitrogen determination in the sample prepared as first stated gave :

	Calculated for $C_{14}H_{12}N_2O$.	Found.
N	12.50	12.53

In order to determine whether this compound is identical with that obtained by Pinner, we have prepared the substance by dissolving benzonitrile in fuming sulphuric acid, according to his directions, and have found that the compound thus obtained also melted sharply at 100° to 101°. A crystallographic examination of the two products was made by Mr. C. H. Warren, to whom the authors wish to express their thanks for the following report : "A trial on the reflection goniometer showed that the faces gave poor reflections, consisting of a number of faint signals for each face, and that a full description was not practicable. However, enough measurements were made of the same zone on both lots of crystals to show satisfactorily the identity of the two specimens. The crystals

[1] *Loc. cit.* [2] J. prakt. Chem., 30, 90.

show monoclinic symmetry. The forms observed were *c* 101 (?), *y* $10\bar{1}$ (?), and *m* 110, probably. On many of the crystals the edges between the prism and top faces were highly modified. The measurements of zone $c \wedge y$ were as follows:

	Ours.	Pinner's.
$c \wedge y$	49° 9′	49° 10′
$y \wedge c'$	130° 51′	130° 40′

The angles measured agree closely considering the poor quality of the reflections." The crystallographic and chemical properties therefore show that the two products are identical. On warming the hydrochloric acid solutions, both products give dibenzamide.

Benzoylbenzamidine hydrochloride, $C_6H_5C(NHCOC_6H_5)(Cl)(NH_2)$.—

The above amidine was dissolved in benzene containing some chloroform, and the solution was saturated with hydrogen chloride, when a heavy, thick oil separated. This oil consists probably of a dihydrochloride. It is very unstable. The material was protected from moisture and dry carbon dioxide was led in, to expel the excess of hydrogen chloride. After a number of hours the material crystallized in small colorless prisms. On pressing on paper it was found to be somewhat sticky. It was then heated to 50° when considerable hydrogen chloride escaped, and the mass became a sandy powder. Thus obtained it melted, not sharply, at about 190°, and a chlorine determination gave the following:

	Calculated for $C_{14}H_{13}N_3O.Cl$.	Found.
Cl	13.6	12.9

This salt is readily soluble in water, and decomposes with the separation of dibenzamide.

The *platinum chloride double salt* was obtained by dissolving the amidine in aqueous hydrochloric acid and adding platinum chloride. It separates as a straw-yellow precipitate which darkens on heating at about 225° to 230°, and melts at 240°. A platinum determination gave:

	Calculated for $(C_{14}H_{13}N_3O.HCl)_2PtCl_4$.	Found.
Pt	22.7	22.5

Benzoylethylbenzamidine.—This was prepared by allowing six grams of benzoylbenzimidonormalpropyl ester to stand in alcohol for some time mixed with an excess of a 33 per cent. solution of ethylamine. The alcohol was then evaporated, and it was attempted to crystallize the residue from dilute alcohol, ligroïn, and benzene, but a sharp melting-point was not obtained until the material was dissolved in dilute hydrochloric acid, precipitated by ammonia, and then crystallized from strong alcohol. Thus obtained it separated in beautiful colorless prisms which melted at about 87° to 88°. This compound is undoubtedly identical with the compound obtained by Lossen[1] by acting on ethyl benzamidine with benzoyl chloride. He gives the melting-point as 88°.

Benzoylphenylbenzamidine.—4 grams of benzoylbenzimidoethyl ester were mixed in ether with 1.5 grams of aniline. No evidence of any reaction was noticed after standing over night. The ether was then evaporated, and the residue heated on the steam-bath, when it solidified. The material was found to crystallize beautifully from alcohol, in thick bunches of rhombohedrons apparently. The material is insoluble in cold dilute sodium hydrate and melts at 143°. This gave on analysis :

	Calculated for $C_{20}H_{16}N_2O$.	Found.
N	9.33	9.32

This compound has recently been obtained by Beckmann and Sandal.[2] They find that the compound melts at precisely the same temperature as we do.

When dry hydrogen chloride was passed into a chloroform solution of this acyl amidine, no precipitate resulted. On evaporating the chloroform in a stream of dry carbon dioxide, an amber-yellow varnish remained. When warmed with water this gave a mass of colorless needles or prisms, which melted at 149°, and had all the properties of dibenzamide.

An attempt was made to prepare *benzoylmethylphenylbenz-*

[1] Ann. Chem. (Liebig), **265**, 162. [2] *Loc. cit.*

amidine by acting on benzoylbenzimidoethyl ester with monomethylaniline, when it was found that this secondary aniline did not give an acyl amidine. 4 grams of the acylimido ester and 1.7 grams of methylaniline were heated to 100°, then for some time kept at about 70°, and, finally, after long standing, crystals separated. These crystallized from alcohol in prisms melting at 147°–148°. A nitrogen determination gave:

	Calculated for acylamidine.	Calculated for dibenzamide.	Found.
N	8.91	6.22	6.17

With ethylaniline the same result was obtained. The above analyzed material was soluble in alkali and precipitated again by acids; it was therefore dibenzamide.

Acetylphenylbenzamidine.—When acetylbenzimidoethyl ester is mixed with aniline and allowed to stand, the mixture solidifies. On crystallizing from 95 per cent. alcohol, it forms stout, colorless crystals, which melt at 138°.5. A nitrogen determination gave:

	Calculated for $C_{15}H_{14}N_2O$.	Found.
N	11.76	11.94

Acetylparatolylbenzamidine.—*p*-Toluidine and acetylbenzimidoethyl ester were mixed in molecular proportions and allowed to stand, when the mixture soon solidified. The material was crystallized from 50 per cent. alcohol, when it was found to melt at 136°.5. A nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O$.	Found.	
		I.	II.
N	11.11	11.30	11.30

Acetylmetachlorphenylbenzamidine.—1.5 grams of acetylbenzimidoethyl ester and 1 gram of metachloraniline on mixing solidify after some time. The material crystallized from alcohol separates in clusters of colorless needles or prisms. It melts at 128°–129°. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}N_2OCl$.	Found.
N	10.27	10.08

A portion of the analyzed material was dissolved in dry benzene, and the solution was saturated with hydrogen chlo-

ride, when a sticky precipitate separated. The excess of hydrogen chloride was expelled by means of a current of dry carbon dioxide. The precipitate, unsuitable for analysis, dissolved readily in water, and, on warming up to 80°, colorless needles separated. These melted from 118°–119°, (acetbenzamide), and dissolved readily in dilute sodium hydroxide. The solution on standing deposited plates (benzamide).

2,4-Xylylbenzamidine.—When 2,4-xylidine and acetylbenzimidoethyl ester were mixed and allowed to stand a long time, a solid separated. The material was too soluble to crystallize from alcohol. The alcoholic solution was precipitated with dilute potassium hydrate, in order to remove any acetbenzamide, when an oil separated. This, on standing, solidified to a mass of prisms. The material was readily soluble in warm ligroïn, and crystallized in long, colorless needles, melting at 106°. Nitrogen determinations showed that this is not the expected acetyl-2,4-xylylbenzamidine, but that the acetyl group had been removed.

	Calculated for acylamidine $C_{17}H_{18}N_2O$.	Calculated for amidine $C_{15}H_{16}N_2$.	Found. I.	Found. II.
N	10.52	12.50	12.34	12.36

The material dissolved readily in dilute hydrochloric acid and gives a yellow precipitate with platinum chloride.

Acetyl-β-naphthylbenzamidine was formed when β-naphthylamine was warmed with acetylbenzimidoethyl ester. The product was crystallized from 95 per cent. alcohol, when it melted at 137°. A nitrogen determination gave:

	Calculated for $C_{19}H_{14}N_2O$.	Found.
N	9.72	9.64

Propionylphenylbenzamidine.—When propionylbenzimidoethyl ester was mixed with aniline, the mixture solidified in about four or five hours. It was crystallized from alcohol, when small, stout prisms of a yellowish-white color were obtained. These melt at 138°, and a nitrogen determination gave:

	Calculated for $C_{16}H_{16}N_2O$.	Found.
N	11.11	11.01

Dry hydrogen chloride led into a benzene solution of this acylamidine gave a sticky precipitate. It was dissolved in water, and in a few minutes a mass of colorless prisms separated. These melted at 98°, and are propionylbenzamide, which compound we described in a previous paper. On warming this with aqueous ammonia, the material dissolved, and, on cooling, plates of benzamide separated, melting at 128°.

An attempt was made to prepare *normalbutyrylbenzamidine* by dissolving the butyrylbenzimidoethyl ester in dilute alcoholic ammonia in the same manner as benzoylbenzamidine was obtained. The product obtained, crystallized from water, melted at 126°–127°, and a nitrogen determination gave:

	Calculated for butyrylbenzamidine.	Calculated for benzamide.	Found. I.	Found. II.
N	14.7	11.57	11.71	11.74

The material thus obtained had all the properties of benzamide. It was found later that acetylbenzimido and propionylbenzimido esters by a similar treatment also give benzamide.

Normalbutyrylphenylbenzamidine. — Butyrylbenzimidoethyl ester reacts with aniline on warming, and the solid thus obtained on crystallizing from absolute alcohol separated in the form of colorless prisms and melted at 137°. A nitrogen determination gave:

	Calculated for $C_{17}H_{18}N_2O$.	Found.
N	10.52	10.53

An attempt to prepare *normalbutyrylmetanitrophenylbenzamidine*, by warming metanitraniline and butyrylbenzimidoethyl ester in molecular proportions, resulted in the formation of a yellow varnish, which has stood for months without depositing crystals. Acetylbenzimidoethyl ester combines with isobutyl amine, and propionylbenzimidoethyl ester combines with allyl amine. Heat is evolved in both cases. The products formed are oils which have not been further investigated.

NEW HAVEN, May, 1898.

LXV.—ON A NEW FORM OF WATER BLAST.

By Bertram B. Boltwood.

Various forms of apparatus have been devised for supplying compressed air to blast-lamps, small gas furnaces, etc., where relatively small volumes of air at low pressures are required. Of those forms which make use of the action of a small jet of water, one designed by Richards, and another described by Muenke, have found the widest application. Both of these appliances operate on the injector principle. A small jet of water is projected through the narrow orifice of a tube of gradually increasing diameter. The jet of water sweeps with it a considerable volume of air, which, together with the water, passes into a receiver, where the two are separated. The efficiency of this action is increased by the introduction of a projecting step in the injector tube, or by giving the form of an undulating curve to the tube itself. This deflects the jet, diminishing its velocity and causing it to completely fill the tube.

The effectiveness of this form of apparatus is, however, limited. This follows as a necessary result of the system upon which it is constructed. The orifice through which the jet passes must, of course, have a greater cross-section than the jet itself, for otherwise no air would be drawn through it. If the size of the orifice be increased beyond this, the efficiency reaches a certain maximum, beyond which any further increase in the size of the orifice causes a reduction in both the pressure and the volume of the air supplied. With the maximum free space, which must necessarily be small, for the admission of air, about the circumference of the jet, the friction experienced by the air in passing must be very considerable.

In the blast which is here described the objectionable features mentioned above have been done away with, and as a result the efficiency of the apparatus has been greatly increased.

The essential parts of the apparatus are the following: The receiver *A*, having the form of a cylinder 8 inches in height and 6 inches in diameter, divided into three compartments, *b*, *c*, and *d*, by the partitions *p* and *p'*, there being a

circular opening 2 inches in diameter between *b* and *c*, and two smaller openings between *c* and *d* (as shown in Fig. I.); the injector tube *l*, $7\frac{1}{2}$ inches long and $\frac{5}{8}$ inch outside diameter, provided at the top with the small funnel-shaped projection *g*; the outlet tube *f*, having a diameter equal to that of *l*, extending upward from *c* and curving over and downward

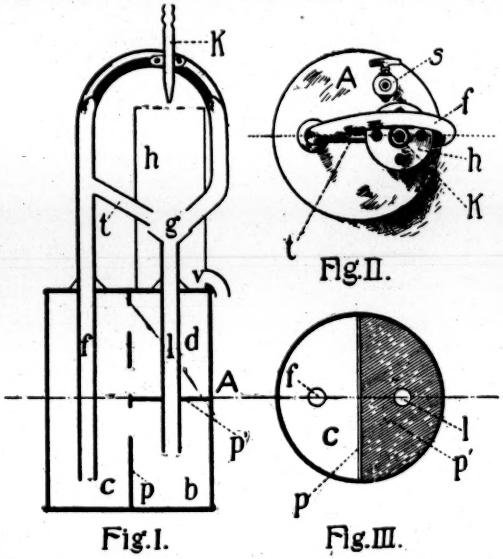


Fig.I. Fig.II. Fig.III.

to *g*; the tube *t* ($\frac{1}{16}$ inch in diameter) opening into *f* and extending to *g*; the stop-cock *s* opening into *d*; and the nozzle *k*, having an orifice $\frac{1}{16}$ inch in diameter, attached to the upper part of the tube *f*. The upper part of the tube *f* is bent slightly out of the plane of section in order that the axis of *k* and *l* may *exactly* coincide.

The action of the blast is as follows: The cock *s* is opened and the water is turned on. The jet of water issuing from *k* passes through *l* and falls into the compartment *b*. When

the level of the water in *b* rises above the lower end of the tube *l* a considerable volume of air is swept into *A*. This air escapes through *f* and *s* and later through *s* only. The water flows from *b* into *c* through the opening in the partition between them. The cock *s* is now closed and the increase of pressure in the receiver causes the water to be forced up through *f* and into *g*. The jet from *k* now strikes upon the surfaces of the water in *g* and sweeping with it a large volume of air, drives it downward into *A*. If the cock *s* be now opened, a stream of air of a volume and pressure sufficient to supply a large blast-lamp will be obtained.

The manipulation of the apparatus in practice is extremely simple. The proper adjustment of *s* for giving the maximum efficiency is readily determined. A glass water-gauge attached to the outside of *A*, and connected with the compartment *c*, is very convenient, but not at all necessary. Spattering is prevented by surrounding *g* with a cylindrical case *h*, having openings in the top to allow the entrance of air, and an overflow pipe *v*, for the escape of the water. When the blast is set up in a permanent position it is best to place it well below the level of the blast-lamp bench, and to make the connection between the compartment *d* and the stop-cock *s* by means of a pipe at least 1 inch in diameter. This will prevent any water from reaching the lamp, in case *s* is not properly adjusted. When *s* is attached directly to the receiver, as shown in Fig. II., a good-sized bottle inserted between *s* and the lamp will serve the same purpose.

Fig. I. is a vertical section of the complete apparatus; Fig. II. is a projection from directly above; and Fig. III. is a section through the middle of the receiver.

The advantages of this form of blast are: That the orifice offered for the entrance of water and air is of such ample size that any considerable friction is avoided; that the injector tube is perfectly straight and free from any obstruction, so that the jet of water is not deflected and the maximum effect is obtained; and that the energy of the jet is transmitted to a much greater volume of water, which circulates continuously through the apparatus, flowing from *f* through *l* and acting as a piston which completely fills the cross-section of the tube.

Two points of construction are absolutely essential to the satisfactory working of the blast. The shape of the nozzle *k* must be such that the jet of water igniting from it is perfectly cylindrical and unbroken for at least 15 inches of its length, and the jet must pass *exactly* through the longitudinal axis of the tube *l*. The latter requirement is most easily assured by leaving the attachment of the bottom of the receiver until the last, and setting the nozzle so that the jet falls in the proper position.

A number of tests were carried out in order to determine the efficiency of the blast described in this article as compared with that of the blasts of Richards and Muenke. The volume of water consumed and the volume of air furnished was measured in each case. The results are given in the following table:

	Volume of water consumed per minute. Liters.	Volume of air supplied per minute. Liters.	Ratio.
Muenke,	5.1	5.5	1.1
Richards,	6.6	7.2	1.1
New form,	2.7	8.1	3.0

The pressure of the water used was the same in each case and was not more than 100 feet. The air was measured at atmospheric pressure.

This new blast can be obtained from Messrs. Eimer and Amend, of New York City, who have been authorized to carry out its manufacture.

NEW HAVEN, CONN., May, 1898.

LXIV.—ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS. PART I.

By James Locke.

The problems set before the inorganic chemist by the periodic system, which have directly or indirectly guided almost all the inorganic investigations of the past thirty years, may be divided, roughly in the abstract but very sharply in the results obtained, into two classes. The one, of the fruitfulness of which no one can complain, deals with the superficial group-relations which exist between the members of the various families. Their solution leads to what may be called the development of group analogies. The problems of the second class, on the other hand, have either been entirely neglected, or their study has yielded only the most unsatisfactory results. These have had to do with the contradictions of fact which the system, as formulated by Mendeléeff, involved, and to which the system should in course of time adapt itself. But all the more important inconsistencies which it presented in the year 1870 still remain, and are finally recognized as facts which, for the sake of a convenient principle, must not be forced into a conspicuous position. The behavior of the elements of low atomic weight; the appearance of one and the same element in more than one degree of oxidation; the properties of the platinum metals; either receive no expression in the system, or they stand in direct contradiction to its laws. The difficulties involved, however, are confined chiefly to the compounds. The relations between the elements, *as elements*, are in almost every case clearly pointed out in the usual tables. This is true in regard to both the physical and chemical properties of the elements themselves. In this paper, therefore, only that part of Mendeléeff's law will be discussed, which says that the *nature of the compounds of an element is also a function of its atomic weight*.

Of the 65 elements having places in the system, 9 of them, iron, cobalt, nickel, and the platinum metals, are put in a

vertical row by themselves, where they form the so-called 8th family, a family which may be said to fall outside the system proper. In this group many of the regularities which can be traced through other families are wanting.

The valency of the elements increases by one in each successive vertical row of the system, until the fourth is reached, after which each family yields two series of compounds, the one of increased, the other of decreased valency. In the potassium-nickel series, for instance, the various elements should enter into compounds with the valencies :

$$K^{I}, Ca^{II}, Sc^{III}, Ti^{IV}, V^{V}, Cr^{VI}, Mn^{VII}, (Fe, Co, Ni)^{VIII}.$$
$$V^{III}, Cr^{II}, Mn^{I}.$$

So, since chromium falls within the 6th family, the greatest weight is laid upon the fact that chromic acid and its salts show such close analogy to sulphuric acid and the sulphates. The fact that potassium permanganate is isomorphous with the perchlorate, and like the latter only sparingly soluble in cold water, likewise assumes the utmost importance. If compounds of iron, cobalt, and nickel were known, in which these elements were octavalent, they, too, would possess the greatest theoretical value. But, with the exception of nickel carbonyl, a doubtful case of octavalency, these theoretically necessary compounds have never been obtained. Up to the present no one has succeeded in getting beyond the ferric acid of hexavalent iron.

That the decrease in valency, on the other hand, must stop before the 8th family is reached, is obvious, for the 7th family is itself univalent, and a further decrease would prevent iron, cobalt, and nickel from forming any compounds at all. But this regularity ceases still further on,—with chromium. No univalent manganese compounds have been obtained. Now, inasmuch as the iron, cobalt, and nickel compounds fail to conform with a regularity which can otherwise be traced throughout the entire sytem, they are assigned an entirely different rôle from that of other elements. They form transition stages, so to speak, from the manganous salts to the copper compounds of the next horizontal row. But this transition is not from the compounds of univalent man-

ganese to those of univalent copper. Univalent manganese is unknown. It is from divalent manganese to divalent copper—to copper in a degree of oxidation which in no way corresponds to the position of this element in the system, and the salts of which have nothing more in common with the cuprous compounds, than has sulphuric acid with hydrogen sulphide; the same element can be obtained from both, and even then the road is by no means a smooth one, for directly before manganese stands chromium, and since divalent manganese has no place in the system, the chromous salts must be regarded as the true starting-point for the transition. But the transition from the unstable divalent and stable trivalent derivatives of chromium to those of ferrous and ferric iron is through a manganese in which the relative stability in the two degrees of oxidation is exactly the reverse.

I know I lay myself open here to the charge of expecting too much from the system. But why? Here is a great law of nature, the correctness of which no one can doubt. But in order to illustrate this law, an empirical arrangement of the elements is formed, and this arrangement we are all too apt to confuse with the law itself. The periodic system is satisfactory enough for the elements. Lothar Meyer's curves of the atomic volumes and melting-points prove this. For the compounds it is *unsatisfactory*. And in order to find out how the law does apply to compounds, we must sift out and discuss the discrepancies which the system shows in regard to them.

As with iron, cobalt, and nickel, so it is with all the other members of the 8th group. These metals, at the time of the promulgation of the periodic system, were assigned a position which, satisfactory though it was in illustration of their properties as elements, was in regard to their compounds absolutely abnormal; and no amount of investigation and speculation, with the periodic system as a basis, can clear up the contradictions which their position entails.

A second point upon which no light has been thrown lies in the behavior of the so-called "typical elements." These, as Ostwald remarks, instead of being types of the families at the head of which they stand, have in the majority of cases

properties directly at variance with those of the other members of their respective groups. In his "Principles of Chemistry" Mendeléeff says: "The elements of the first two series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of a group, still they show many peculiar and independent properties. These lightest elements are:

H;
Li, Be, B, C, N, O, F;
Na, Mg, .., .., .. "

As Mendeléeff left these elements, "typical," so they have remained, and the history of thirty years contains no mention of a successful attempt to unite them more closely than by that ill-fitting word to the groups to which they should show analogies.

Lithium is the lightest of all the elements having places in the system. It should, therefore, from the above, have the greatest number of independent properties of any of the typical elements. Or, one should at least expect to find metallic lithium and lithium compounds varying from the higher alkali metals and their derivatives in one and the same degree, since their departure from the rest of the group is conditioned by one and the same cause. The abnormal behavior of the other typical elements should be along the same lines as in the case of lithium and its compounds. The essential properties of metallic lithium stand in strictest analogy to those of the other alkali metals. Metallic beryllium fits in accurately in the series formed by magnesium, zinc, cadmium, and mercury. Between boron and aluminium the analogy is less clear; but it appears again in full force in the properties of free carbon and silicon. The two elements show in their physical properties, allotropic modifications, and indifference to reagents, the strongest similarity. Fluorine and chlorine, in the elementary state, present the most striking analogies; and the gradations in character which the free halogens undergo with increasing atomic weight, from fluorine through to iodine, yield one of the most perfect chemical series imaginable.

Of the 7 elements making up the first horizontal row, therefore, at least 4 possess, *in the elementary state*, properties closely akin to those of the subsequent elements in their respective families, and complete the series which the latter form.

Now, if the periodic system is true for compounds as well as for the elements themselves, then the compounds of analogous elements must be analogous—a simple deduction from the law which is not altered in its bearing, by the fact that the elements with which we happen to be dealing fall within the so-called typical class. If the low atomic weights, therefore, of the four elements, lithium, beryllium, carbon, and fluorine, are not of such influence as to prevent their ranking as they should, in their respective families, we must expect that their compounds will also show analogy to those of the other members of their groups. The compounds of lithium vary more or less from those of the other alkali metals, it is true; its phosphate and carbonate, especially, are less soluble; but, nevertheless, the lithium salts in general possess the characteristics of alkali derivatives, to an extent which would certainly prevent anyone from considering lithium as anything but an alkali metal. Carbon and silicon likewise bear close relationship in their compounds. The property of carbon which gives rise to organic radicals and the existence of such a multitude of combinations between but a few elements, the ability of the carbon atoms to unite with one another, likewise appears in silicon. The silicon hydrides, the various chlorides, bromides and iodides, silicon-chloroform, and the complex oxygen compounds, such as silico-oxalic and meso-oxalic acids, illustrate fully the strong similarity between the influence of tetravalent carbon and that of silicon upon their compounds.

The law, and its expression by the periodic system, therefore, holds good in the case of lithium and carbon, and no fault can be found with the typical behavior of the two elements. Now, if the effect of small atomic weight upon both lithium and carbon, is too slight to cause in the nature of their compounds any great variation from that of their homologues, one has a perfect right to assume that this separating influence will not be greater in an element which, in

its atomic weight, lies between the two; but, after a comparison, unprejudiced by the fact that an analogy between the compounds of beryllium and magnesium is required by their positions in the system, can a single trace of true resemblance be found between them, or between beryllium derivatives and those of any other element in the second vertical row? Magnesium hydroxide and beryllium hydroxide are both dibasic, it is true. But there the similarity ceases.

A strongly distinctive feature of all magnesium, zinc, and cadmium salts is seen in their behavior toward ammonia and ammonium salts. They also have a pronounced tendency to form double salts with the compounds of other metals. Their oxides are insoluble in water, but soluble even in weak acids. Calcium, strontium, and barium, on the other hand, are characterized by their soluble, strongly alkaline hydroxides, by their difficultly soluble sulphates, and by the difficulty with which they enter into double salts. These are group characteristics, the presence of any one of which indicates the others. They give a tone to, and define the nature of, all the compounds of the two series. But to beryllium salts not one of them applies. Similar to magnesium though the metal be, its compounds show perfect indifference to ammonium salts; they form no double salts,[1] and the oxide is practically insoluble even in strong, hot acids; as little soluble, in fact, as alumina. This last fact, together with the ready solubility of the sulphate and of the fluoride, and the insolubility of the sulphide, etc., prevent any comparison of the beryllium compounds with those of the alkaline earths.

With fluorine, the nature of the compounds of which it will be unnecessary to discuss in full, the case is similar, although its atomic weight is nearly three times as great as that of lithium. The properties of the free element show it to be a pronounced halogen, with characteristics which one would expect to find in a halogen of lower atomic weight than chlorine. But its compounds are not only widely different from

[1] Certain double fluorides must be noted as exceptions to this statement. The double sulphates, phosphates, etc., known, may be disregarded, as they can be represented by simple constitutional formulas, and this formation is of less significance than that of double halogenides, and the like. Both calcium and strontium yield double sulphates.

those of chlorine, but they often vary in a direction contrary to that of the gradations observed in the rest of the series. Fluorine, it is true, forms in common with the other halogens an acid of the type HR. But in distinction from hydrochloric, hydrobromic, and hydriodic acid, hydrofluoric acid has a remarkably low molecular conductivity; and its salts, in the majority of cases, have properties which are directly the opposite of those of the chlorides, bromides, and iodides. The most pronounced chemical characteristic of the halogen acids certainly lies in the solubility of their salts with heavy metals, and the insolubility of the silver, cuprous, and mercurous compounds. The *fluorides* of silver and mercury, on the other hand, are readily soluble: those of calcium, strontium, barium, magnesium, manganese, iron, cobalt, nickel, chromium, cadmium, copper, bismuth, lead, and others are either sparingly soluble or dissolve only in an excess of hydrofluoric acid. In the readiness with which fluorine enters into metallofluoric acids is seen another great distinction from the other halogens. In this, as in many of its other properties, it approaches very closely to cyanogen. Hydrofluoric and hydrocyanic acids and their salts have, in fact, little more in common with hydrochloric, hydrobromic, hydriodic acids, and the halogenides, than the fact that they are monobasic or derivatives of monobasic acids.

We have, therefore, in lithium, beryllium, carbon, and fluorine, four typical elements which in the free state, *as elements*, stand in close relationship to the other elements of their respective groups. In two of them, lithium and carbon, the influence of their low atomic weights is not such as to deprive their compounds of the chemical nature which characterizes the derivatives of their analogues. The others, although one of them lies *between* lithium and carbon, and the other has an atomic weight almost large enough to take it out of the typical class, fail to show analogy to their homologues; that is, to satisfy the requirements of the system, as soon as they pass from the free state into combination.

These are contradictions which even the mysterious influence of a low atomic weight will not explain. They were known in 1870, and they stand to-day. With the develop-

ment of organic chemistry, and the increase in the number of bodies known, which could not be explained by the laws of valency alone, stereochemistry appeared. Molecular compounds have been the subject of numerous theories, of which one at least, that of Werner, promises to bear fruit; but the inconsistencies shown, in reference to the other elements, by those of low atomic weight, the exceptions to a law more far-reaching than that of valency itself, have remained untouched, simply in recognition of the fact that it was hopeless to look for any explanation for them, which could be reconciled to the system. And why? Because the inorganic chemist, in standing upon the periodic system, has been unable to dissociate in his mind the chemical compound from the elements of which its formula contains the symbols.

Of the work done in the development of group analogies, little need be said. This has been the only successful field of investigation which the formulation of the system opened. But it may be well to point out briefly certain inconsistencies which are involved in the development of these analogies between neighboring metals in the horizontal rows.

One of the pronounced features of the periodic system is the regularity with which the valency of the elements increases in the successive vertical rows—a regularity to which in fact so much importance is attached, that Mendeléeff can say without fear of criticism, "PbO_2 is the normal salt-forming oxide of lead, as are Bi_2O_5, CeO_2, TeO_3 of bismuth, cerium, and tellurium!" According to Mendeléeff, when an element forms two series of compounds, as copper, for instance, in one of which it has the same valency as its neighbor in the horizontal row, its compounds in this degree of oxidation must be similar to those of its neighbor. This rule is well illustrated in the case of copper, for the cupric compounds do bear a very close resemblance to those of the next element, zinc. But examine the rule in its full extension. The formation of an alum by any trivalent metal is rightly regarded as characterizing its behavior throughout all its compounds in this degree of oxidation, and sharply distinguishes its sesquioxide from those of another great class of elements, the rare-earth metals. Associated with the formation of alums is the behavior of the

cyanides toward potassium cyanide. All the sesquioxides[1] which form alums yield soluble double potassium cyanides, the great majority of which have the formula $K_3V(CN)_6$.

In the series,

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni,

the most typical double cyanide is formed by iron; that of cobalt is also stable, and on the other side we find an analogous salt formed by manganese, "owing to its proximity to iron." But chromium, beyond manganese, also forms one; and from some experiments which I myself have made, I find also that potassium vanadicyanide, $K_3V(CN)_6$, is not only capable of existence, but a well-defined compound. We have here the character which the atomic weight 56 lends to the compounds of trivalent iron exerting an influence upon that of one element to the right and three elements to the left. With the alums the case is still more remarkable. These bodies are formed by cobalt, iron, manganese, chromium, vanadium, and titanium; or by six of the ten elements in the row. And not only that; scandium, the metal next to titanium, not only forms a sesquioxide, but this is its only degree of oxidation. Its compounds, however, have the properties characteristic, not of ferric and aluminium salts, but of the rare earths. And, nevertheless, the close proximity of this element to titanium does not lend to the trivalent compounds of the latter a single one of the properties of the rare earths. We must seek the influence to which their character is due far over at the edge of the table.

In the foregoing pages no attempt has been made to criticise the analogies which exist, in the various series, between the elements themselves. With this feature of the system little fault can be found. The alkali metals, the alkaline earth metals, Be, Mg, Zn, .., Ge, Sn, Pb, are thoroughly similar among themselves, and well illustrate the gradation in properties with increasing atomic weight. But with the compounds the case is entirely different. The derivatives of typical elements show no regularity—even in their abnormal

[1] The only exception is in the case of aluminium, the cyanide of which is decomposed by water. Potassium cyanide precipitates the hydroxide.

behavior; the compounds of the 8th group have a decidedly anomalous position. The similarity between the derivatives of elements in states of oxidation uncalled for by the system, either cannot be explained at all, as in the case of lead and barium, magnesium and manganese compounds, or we are forced to ascribe to one or the other series a certain vague, transitive nature. The reason for this lies, not in the principle that the chemical nature of an element and its compounds is a function of its atomic weight, but in our failure to recognize the two-fold character of this principle. We attempt to apply one and the same expression of the law to both elements and compounds. But one has no right, in the systematization of one class of substances, to impose upon himself restrictions which arise only from the system which he employs for another class. No arrangement of the elements according to their atomic weights can be made, which expresses the analogies between the elements themselves, and in which, for instance, magnesium and manganese receive analogous positions. And the result is that, in order to emphasize the relation between zinc and magnesium, which such an arrangement does exhibit, the adherent of the periodic system deliberately closes the door to an explanation of the far closer analogy between the compounds of magnesium and manganese, as if the latter were not conditioned by an equally important law of nature.

A system for the compounds, founded upon the atomic weights of the elements, must also necessarily lead to confusion from another source, for the investigation of the compounds is undertaken solely to characterize the *general chemical nature* of the element. Thus, little distinction is drawn between reactions which do not involve a change in degree of oxidation and those which do. If the two are separated at all, it is only when the resulting compounds are very stable, or else conform to the position of the element in the periodic system. To cuprous compounds, though they are unstable, great importance is attached, because copper belongs to the first family. But, even in so full and scientific a text-book as that of Mendeléeff, the salts of trivalent manganese are reviewed with little more than the passing remark that

they somewhat resemble ferric compounds, and that the chloride decomposes when its solution is warmed. The latter fact seems to deprive the manganic salts of all theoretical interest.

But in a comparison between the derivatives of two metals in the same degree of oxidation, the question of *existence* becomes of more importance than stability, for the latter is often dependent entirely upon external conditions. The fact that bromine is liquid, iodine a solid, at ordinary temperatures, does not prevent the most important analogies being drawn between the physical properties of the halogens in the same state of aggregation, though to obtain bromine and iodine as gases, heat must be employed. So it is with many compounds. They may perhaps be obtained only under, for us, extraordinary conditions, but their very existence may point out in the constituent elements properties which we should otherwise never expect. As an example of such a case only the newly discovered alums of vanadium need be mentioned. The existence of these bodies shows that in spite of the similarity between phosphates and vanadates, the vanadium atom exerts upon the nature of its trivalent compounds the same influence as does iron upon that of the ferric salts. A vanadic solution absorbs oxygen with great avidity, and is therefore called very unstable, but the presence of oxygen is an arbitrarily imposed condition. If oxygen were a rare element, the trivalent salts of vanadium would probably be regarded as its normal compounds, and a vanadate looked upon very much as we look upon ferric acid to-day.

The chemical behavior of an element in a given degree of oxidation must be characterized along two lines. First, by the study of its compounds as mineralogical specimens, their composition, physical properties, solubility, volatility, and the like, together with the reactions which they show without involving change in the degree of oxidation. Secondly, by its passage from this degree of oxidation into others. The first is, in my opinion, by far the more important, for the properties of the compounds of an element in two different degrees of oxidation differ absolutely from one another; and in the two the element appears in entirely different rôles. It

is only after we have ascertained in how far the element can alter its *apparent* character, in corresponding with entirely different elements in different degrees of oxidation, that we can solve its *true* character, and find out a general law for its behavior in all its compounds; and this can be ascertained only by a careful comparison of its compounds with those of other elements in the same degree of oxidation.

A classification based upon this principle, of course, presents great difficulties, owing to the very unsatisfactory extent to which the elements in their unstable degrees of oxidation have been investigated. A thorough study of the compounds, however, has shown that it is capable of giving most interesting results, the nature of which I will discuss in my next article on the subject.

LXV.—THE ACTION OF SULPHUR UPON METALLIC SODIUM.

By James Locke and Alfred Austell.

Among the various investigations which have been published regarding the action of sulphur upon metallic sodium, but one is of recent date. Rosenfeld,[1] in a short article relating to the reactions of sodium, confirms the observations of Davy, Gay-Lussac, and Thenard, that the two combine with nearly explosive force, even at the ordinary temperature. Rosenfeld seems to have made no analysis of his reaction-products, but says that by mixing finely divided sodium, sulphur, and sodium chloride together, and rubbing, he obtained a violent reaction, in which a mixture of the monosulphide and polysulphides was formed. His work is accordingly given in the various reference books as indicating a method for preparing sodium monosulphide.

Through a chance observation made while preparing sodium sulphide in some other work, we have been led to study this reaction more closely. As it is practically impossible to separate the products from any sodium which may have been left unaltered in the reaction, a quantitative investigation of their composition is extremely difficult, and

[1] Ber. d. chem. Ges., **24**, 1658.

our results are therefore only approximate. They indicate conclusively, however, that the monosulphide cannot be formed by the direct combination of sodium and sulphur at temperatures below 220°.

Our method of procedure was as follows: A small weighed quantity of clean sodium was covered with about 50 cc. of dry toluene, and the latter heated until the sodium fused. This was carried out in a small flask fitted with a return-condenser and a separatory-funnel. Through the latter the calculated quantity of sulphur, dissolved in hot toluene, was slowly added, while the contents of the flask were kept briskly boiling. The reaction at first results only in a thin yellow film of polysulphide[1] being formed upon the surface of the sodium. It soon grows violent, however; the sodium swells up, and a porous cake of the compound is formed. After this main reaction, which lasts but a few seconds, has subsided, the rest of the sulphur solution was added rapidly, and the mixture boiled for about an hour. The product was then filtered, washed with hot toluene, dried, and tested for sodium. The presence of uncombined sulphur in the mother-liquid could readily be seen from the yellow color of the latter. When no free sodium was found, the substance was submitted to analysis.

Experiments were made successively with two grams of sodium and the quantities of sulphur calculated for the compounds Na_2S, Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5. The results are tabulated below:

Ratios. Na : S.	Sodium. Grams.	Sulphur. Grams.	Product.	Filtrate.
2 : 1	2.0	1.39	Yellow, mixed with much Na	Colorless
2 : 2	"	2.78	"	"
2 : 3	"	4.17	Traces of Na	"
2 : 4	"	5.56	No Na	Yellow
2 : 5	"	6.95	"	"

According to these results the only compound formed at 110°, the boiling-point of toluene, should approximate rather

[1] The fact that this film is yellow shows that even when a great excess of sodium is present no monosulphide forms, as the latter has a red color. In every experiment made, a greenish-yellow product was obtained.

closely to the formula Na_2S_3. That no lower sulphide is formed is clear, and at this temperature metallic sodium has apparently no action upon the polysulphides. In the first two experiments, as the toluene cooled down, the globules of sodium left showed in fact a bright metallic luster. The products of the last two experiments, in which there was no residual sodium, were analyzed by conversion into the sulphate. They had practically the same composition, with 28.89 and 28.57 per cent. sodium respectively. The percentage of sodium calculated for the compound Na_2S_3 is 32.32, and for Na_2S_4, 26.44. Both products were therefore probably mixtures of these two compounds. That more or less of the higher sulphide is formed is also indicated by the fact that the product obtained in the third experiment ($Na : S = 2 : 3$) contained a small quantity of free sodium.

An experiment was also made in which naphthalene was substituted for toluene, a temperature of 218° being thus obtained. It seemed probable that at this heat a compound containing less sulphur would be formed, if only by the action of sodium upon the polysulphides after the first reaction had taken place. This turned out, however, not to be the case. 2.78 grams sulphur were dissolved in toluene, and added to 2 grams sodium under hot naphthalene. The small quantity of toluene was then distilled off, and the naphthalene kept boiling for an hour. The product contained apparently as much free sodium as that obtained with a mixture of the same proportions at 110°.

NEW HAVEN, CONN., May, 1898.

LXVI.—ON SOME COMPOUNDS OF TRIVALENT VANADIUM.

BY JAMES LOCKE AND GASTON H. EDWARDS.

The green solution obtained when vanadic acid is reduced by nascent hydrogen has been but very slightly studied. That it contains salts of vanadium in the trivalent state was recognized by Roscoe[1] in the course of his elaborate investigation on the chemical nature of this element. Roscoe, however, made no attempt to study the products which could be

[1] Ann. Chem. (Liebig), Suppl., 7, 78.

obtained from the solution which he prepared by dissolving the anhydrous chloride, VCl_3, in water, and failed to make any comparison between that body and the chlorides of other trivalent elements.

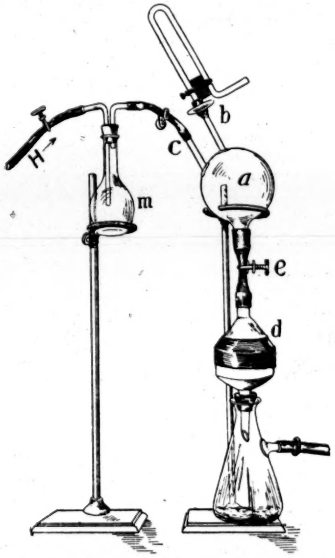
The first compounds to be isolated from a vanadic solution were prepared by Petersen,[1] who examined in a very thorough manner the fluoride and its double salts with the fluorides of other metals. His results pointed to a close resemblance between vanadium sesquioxide and its derivatives and the compounds of the groups formed by aluminium, chromium, manganese, and iron. Thus, the compound $K_2VF_5.H_2O$ exhibits in its general properties, solubility, etc., close similarity to the analogously constituted salts of aluminium, iron, chromium, and manganese. Ammonium vanadifluoride, $(NH_4)_3VF_6$, is isomorphous with the ferric salt, $(NH_4)_3FeF_6$, described by Marignac,[2] and Petersen prepared other members of the series in $(NH_4)_3CrF_6$ and $(NH_4)_3AlF_6$. A similar relation was observed between double salts with the fluorides of divalent metals, such as $CoVF_5.7H_2O$, $CoCrF_5.7H_2O$, etc.

Petersen's work and the conclusions drawn from his results were further substantiated by the recent investigations of Piccini[3] on the alums of vanadium. He succeeded in isolating the salts $NaV(SO_4)_2.12H_2O$, $KV(SO_4)_2.12H_2O$, $NH_4V(SO_4)_2.12H_2O$, $RbV(SO_4)_2.12H_2O$, $CsV(SO_4)_2.12H_2O$, and $TlVSO_{42}.12H_2O$. With the exception of a short article by Brierly,[4] who prepared a vanadium sulphuric acid, or 'alum acid,'[5] $V(SO_4)SO_4H.4H_2O$, the above investigations embrace practically all that has been published on vanadic salts.

We have recently undertaken the preparation of a number of other compounds, the analogues of which are of characteristic nature in the case of chromium, in the hope of ascertaining more definitely the influence which the atomic weight of vanadium exerts upon the development of the properties common to the compounds of the group: aluminium, vanadium, chromium, manganese, iron, and cobalt.

[1] J. prakt. Chem. (2), **40**, 44 (1889). [2] Ann. chim. phys., (3), **60**, 306.
[3] Ztschr. anorg. Chem., **11**, 106; **13**, 441. [4] J. Chem. Soc. (London), **49**, 822.
[5] Chromium is the only other alum-forming metal which yields such an acid, $Cr(SO_4)SO_4H$.

The chief difficulty which an investigation of this kind presents lies in the extreme readiness with which vanadic solutions absorb oxygen, with formation of vanadyl salts. Petersen was able to start directly from the anhydrous sesquioxide, which is soluble in hydrofluoric acid. The solutions of vanadic sulphate used by Piccini in the preparation of the alums were obtained simply by the electrolysis of vanadic acid



in a solution of sulphuric acid. These methods, while satisfactory in individual cases, are of course limited in their applicability, and they could not be used in the preparation of such compounds as a vanadicyanide, sulphocyanate, or the like. We were therefore compelled to start out from the readily oxidizable vanadic hydroxide, precipitated by an alkali after the reduction of the pentoxide with sodium amalgam.

In order to protect the hydroxide and solutions from oxida-

tion, all operations were carried out in an atmosphere of hydrogen. For this purpose the apparatus shown in the accompanying figure was employed. The pear-shaped bulb *a*, of which we had several pieces, holds about 500 cc. Over its drawn-out end, which is two-thirds of an inch in diameter, passes a piece of thick-walled, soft-rubber tubing, which can be closed by a stop-cock *e*. The tube *b* is of capillary diameter, fitted with a glass cock, and bent over on itself, to more securely prevent the entrance of air when this cock is open. *c* is a somewhat wider tube, which serves for the introduction of reagents, and is closed by a stop-cock when necessary.

For heating on the water-bath, the bulb is placed on the latter, mouth downward, while a rapid current of hydrogen is passed in at *c*, *a* being open. The contents of the bulb may be boiled in a similar manner, the bulb then resting on its side. Reagents are added by means of a small flask *m*, fitted with a cork holding two short tubes, one of which is connected with the hydrogen generator. The reagent having been introduced into the flask (a test-tube is also convenient) the air in the latter is displaced by hydrogen, and the second tube then connected with *c*. The flask is then simply inverted, whereupon the reagent runs into the bulb.

The most important and difficult operation involved in the work was of course the filtration and washing of the vanadic hydroxide. To perform this without exposing the substance to the air, a Buchner's funnel was used, to which was joined by a wide rubber band a well-fitting piece of apparatus, *d*, like an inverted funnel. The stem of the latter was of the same diameter as the mouth of the bulb. Before attaching this filtering-apparatus to the bulb, it was entirely filled, together with the suction-flask, with water, and the latter then displaced by hydrogen. Connection was then made, slight suction applied, and the stop-cock at the mouth of the bulb opened. The precipitate was washed with water from which the air had been expelled by boiling, from a flask connected as for the introduction of reagents.

When the next operation involved the solution of the precipitate in an acid, the filtrate was drawn off by suction

through the pump, the suction-flask rinsed with the water from one or two additional washings, and the acid then introduced as above. The solution was then transferred, either to another bulb, or, if it was to be evaporated to crystallization, to a crystallizing-dish, the side tube of the suction-flask being in that case held below the surface of some benzene placed in the dish.

By taking proper care in the observance of minor details, such as the filling of the tubes with water before making connections, etc., we were able almost entirely to obviate the danger of oxidation; and after a little practice we could carry out the operations of filtration and the like almost as rapidly as in the open air. In one afternoon, starting out with vanadium pentoxide, we have prepared vanadium dihydroxide, $V(OH)_2$, washed it, redissolved in hydrochloric acid, and brought the solution into a desiccator. In spite of all the operations subsequent to the reduction of the vanadic acid, the final solution possessed the true lavender color of vanadious salts, without a trace of green or brown. Roscoe describes such a solution as being a more sensitive reagent towards oxygen than is pyrogallol itself.

The vanadium preparations which we used in this work were placed at our disposal through the kindness of Prof. Paul Jannasch, of Heidelberg, Germany. They consisted chiefly of thoroughly purified vanadates of sodium and ammonium. These compounds were worked up as follows: Enough of the substance to yield about 5 grams of vanadium hydroxide was dissolved in a small quantity of water, 10 cc. of concentrated hydrochloric acid were added, and the solution boiled with alcohol to reduce the vanadic acid to vanadyl dichloride, $VOCl_2$. After the alcohol had been driven off, the solution was transferred to a bulb, and while a rapid current of hydrogen was led through the latter, 5 per cent. sodium amalgam was gradually introduced in small lumps, the solution being in the meantime kept acid by the occasional addition of hydrochloric acid. The reduction was continued until the solution just began to lose the pure green color of the vanadic salts and assume a bluish-green tint, due to compounds of the next lower degree of oxidation. The

operation required the addition of about 700 grams of amalgam.

The mercury was next drawn off, the solution filtered, transferred to another bulb, and treated in the cold with just enough ammonium hydroxide to precipitate the vanadic hydroxide[1] completely. The latter comes down as a dirty green flocculent precipitate, which absorbs oxygen with the greatest avidity. It was allowed to stand for some time, and then filtered and washed thoroughly with warm water from which the air had been expelled. From this precipitate the following salts were obtained by solution and crystallization.

Vanadium Trichloride, $VCl_3.6H_2O$.—Halberstadt[2] mentions the fact that when the anhydrous chloride, VCl_3, is dissolved in water and the solution evaporated over sulphuric acid, a very unstable crystalline compound is obtained. Piccini mentions in a foot-note to his first article on the vanadium alums[3] that he had obtained this substance in distinct crystals, and found it to have the above composition. This foot-note escaped our notice when first reading his article, and at the time of preparing the compound we supposed we were the first to have isolated it. As, however, nearly three years have elapsed since his article was sent in for publication, we may be allowed to describe the compound, yielding to him the priority of its discovery.

It is obtained by dissolving vanadic hydroxide in concentrated hydrochloric acid and evaporating the green solution to dryness in a vacuum-desiccator. The salt separates out from the sirupy liquid in large green prisms, some of which attained with us the length of nearly half a centimeter. It dissolves in water with extreme readiness, yielding, like the other neutral vanadic salts, a brown solution which becomes green on acidification. The salt is very deliquescent, and on exposure to the air for any length of time, dissolves in the water absorbed and is oxidized to vanadyl dichloride. It is readily soluble in both alcohol and ether, but no distinct crystals could be obtained from its solution in these liquids.

[1] Potassium hydroxide does not work as well for this purpose, as it dissolves more or less of the vanadic hydroxide.

[2] Ber. d. chem. Ges., **15**, 1619 (1882). [3] Ztschr. anorg. Chem., **11**, 107 (1896).

In the analysis of the substance the solution was acidified with nitric acid and the chlorine precipitated with silver nitrate. The vanadium was determined in another portion by titration from the tetravalent to the pentavalent state with iodine, according to Browning's[1] method. The water was estimated by difference:

	Calculated for $VCl_3.6H_2O$.	Found.
V	19.24	18.96
Cl	40.10	39.95
H_2O	40.66	41.09
	100.00	100.00

An attempt was made to measure the crystals, but they proved too hygroscopic. Their optical properties, however, were found to conform to the rhombic system. Salts of composition similar to that of this compound are seen in $AlCl_3.6H_2O$, $CrCl_3.6H_2O$, and $FeCl_3.6H_2O$.

Potassium Vanadichloride.—An attempt was made to prepare from the chloride a double salt analogous to those of the series $R_2FeCl_5.H_2O$, in which R is K, Rb, NH_4, etc. A few grams of the trichloride were dissolved in concentrated hydrochloric acid, the calculated quantity of potassium chloride added, and the mixture left to crystallize in a vacuum. The product consisted chiefly of green crystals of a somewhat lighter shade than that of the pure vanadium chloride, but it was impossible to isolate these completely. A vanadium determination, made in as pure a product as we could obtain, showed that it contained 22.41 per cent. V. The quantity calculated for the anhydrous compound $KVCl_4$ is 22.03 per cent. V.

Vanadium Bromide, $VBr_3.6H_2O$.—This compound was prepared in a manner strictly analogous to that by which the chloride was obtained, pure concentrated hydrobromic acid being used. It crystallizes with less readiness than the chloride, and decomposes more easily. In other respects the two compounds were closely similar. The bromide decomposes more or less on solution in water, leaving as a residue a small quantity of a brown substance, probably a basic bro-

[1] Ztschr. anorg. Chem., **1**, 158.

mide. Like the chloride, it is soluble in both alcohol and ether, to a green solution. The analysis was carried out as in the case of the chloride.

	Calculated for $VBr_3 + 6H_2O$.	Found.
V	12.83	12.62
Br	60.10	59.65
H_2O	27.07	27.73
	100.00	100.00

The iodide could not be obtained. Vanadium hydroxide dissolves in hydriodic acid as readily as in hydrochloric or hydrobromic, but the solution turns brown on evaporation and eventually leaves only an amorphous, brownish-black residue, only partially soluble in water.

Potassium Vanadicyanide, $K_3V(CN)_6$.—For the preparation of this compound, it was found more convenient to start out from the anhydrous vanadium trichloride, which we prepared according to the method of Halberstadt.[1] About 5 grams of this substance were dissolved in as little water as possible[2] and slightly acidified with hydrochloric acid. A concentrated solution of potassium cyanide containing about one and a half times the calculated quantity of the salt was placed in a bulb, and the vanadium chloride solution then added. The mixture at once assumed the form of a thick, deep-purple paste, which gradually became thin again, though without at first losing its color, and remaining almost opaque. This part of the reaction was observed by Petersen,[3] who states that he thus obtained a dark-blue solution. The blue color, however, is in fact due only to very finely divided particles of the original precipitate suspended in the solution, which is itself of a deep wine color. After shaking for some time, the liquid cleared and only a few flakes of a brown residue, presumably the hydroxide, remained undissolved. It is absolutely necessary to have a considerable excess of potas-

[1] Ber. d. chem. Ges., **15**, 1619 (1882).

[2] The formation of the hydrated chloride is readily seen when a quantity of the anhydrous chloride is added to about its own volume of water. It dissolves with a hissing sound, and, on cooling, the liquid solidifies to a green crystalline mass. On addition of more water, this dissolves to a brown solution.

[3] J. prakt. Chem., **40**, 50.

sium cyanide present, as the precipitate dissolves with great difficulty, and a clear solution cannot otherwise be obtained.

The wine-colored solution, after being filtered, was treated with just enough alcohol to bring about incipient precipitation, and then allowed to stand for some hours surrounded by ice-water. A fine precipitate separated out, which consisted of a mixture of potassium cyanide and vanadicyanide, and in addition to this, comparatively large crystals of the latter collected on the sides and bottom of the vessel. These alone were saved, the rest of the product being removed by lixiviation. The crystals were repeatedly washed by decantation with 95 per cent. alcohol, and finally with ether, and dried in a vacuum-desiccator.

In the analysis of the product the carbon and nitrogen were determined by combustion. The vanadium was estimated by titration with iodine, and the potassium as sulphate, in a separate portion, after the oxidation of the vanadium to vanadic acid and its removal as lead vanadate.[1]

	Calculated for $K_4V(CN)_6$.	Found.
V	15.74	15.89
C	22.22	21.80
N	25.93	26.36
K	36.11	36.47
	100.00	100.52

This salt forms another member of the series of complex cyanides of the formula $K_4M(CN)_6$, of which the other members as yet known are $K_4Cr(CN)_6$, $K_4Mn(CN)_6$, $K_4Fe(CN)_6$, $K_4Co(CN)_6$, $K_4Rh(CN)_6$, and $K_4Ir(CN)_6$. The crystals obtained were about a millimeter in length, and of a bright scarlet color. Owing to their instability it was impossible to measure them, and thus determine whether they were isomorphous with the other members of the series. They appeared under the microscope to be rhombic plates, with well-formed domes and base; in polarized light, however, they showed inclined extinction, and are therefore probably monoclinic like the others. In potassium ferricyanide the angle β is 90° 6′.

[1] Roscoe: Ann. Chem. (Liebig), Suppl., 8, 102.

Potassium vanadicyanide is readily soluble in water, insoluble in alcohol. Its aqueous solution grows turbid within a few minutes, however, but is much more stable when containing some free potassium cyanide. Even in that case it cannot be kept for any length of time. The freshly-prepared solution is at once decomposed by acids, turning green. It gives off a slight odor of hydrocyanic acid, as does the solid salt itself. The solution is at first stable toward alkalies in the cold, but on heating or standing for some time the hydroxide separates out.

The solution yields colored precipitates with the neutral solutions of various metals, of which the following are the most distinct :

Ferrous iron,	red-brown.
Cadmium,	yellow.
Copper,	yellow.
Nickel,	purple.
Manganese,	greenish-yellow.

Silver and mercury salts are reduced by it, with deposition of the metals. None of these precipitates is stable toward acids, and their color soon undergoes a change on standing.

We have made repeated attempts to isolate the purple precipitate which separates on the first addition of potassium cyanide to the vanadic solution, but without success. The compound, probably vanadic cyanide, is extremely unstable and on drying yields a green or brown amorphous product, which is obviously a mixture.

The vanadicyanides of ammonium and sodium seem to exist only in solution. Vanadium cyanide dissolves in excess of ammonium cyanide or sodium cyanide, to solutions of the same color as that of the potassium salt. No crystalline products, however, could be obtained from either solution, either by evaporation or precipitation with alcohol. When the latter is employed the compounds decompose at once, with separation of a thick, blue paste.

The properties and reactions of potassium vanadicyanide are of special interest in view of the relative stability of the complex cyanides of the other metals of the group. The only stable compounds of trivalent cobalt are those which contain

the metal as a constituent of a complex radical, either positive, as in the cobaltiamines, or negative, as in $K_3Co(CN)_6$, $H_3Co(CN)_6$, etc. The corresponding ferric compounds, *in comparison with other ferric salts*, are somewhat less stable than the cobaltic compounds as compared with simple cobaltic salts. Thus, for example, potassium ferricyanide is less stable, compared with ferric sulphate, than is potassium cobalticyanide, when compared with cobaltic sulphate. The complex manganese derivatives are relatively still less stable. Among the latter is a sodium salt, $Na_3Mn(CN)_6$, but the free acid is unknown. Chromic cyanide yields neither an acid, $H_3Cr(CN)_6$, nor a sodium salt, and ammonium chromicyanide[1] is very unstable. The chromicyanide solutions, however, are stable towards alkalies even on boiling. In the case of vanadium, neither the sodium nor ammonium salts can be obtained; potassium vanadicyanide is instantly decomposed by acids, with evolution of hydrocyanic acid, and is stable towards alkalies only in the cold. The simple vanadic salts are comparatively stable. Aluminium, which has the lowest atomic weight of all the metals in the group, is precipitated as hydroxide when potassium cyanide is added to its solution, and no cyanogen compounds at all of this metal can be obtained. The tendency to form complex radicals, throughout the entire group, as compared with the tendency to form simple salts, is thus seen steadily to diminish with a decrease in the atomic weights of its members.

Potassium Vanadisulphocyanate, $K_3V(CNS)_6.4H_2O$.—Among the characteristic compounds of trivalent chromium the derivatives of chromic sulphocyanate are very prominent. Potassium chromisulphocyanate, $K_3Cr(CNS)_6.6H_2O$, is almost as stable as the chromicyanide. It is not decomposed by either alkalies or acids in cold solution.[2] A number of other salts, such as $Ag_3Cr(CNS)_6$, $Ba_3[Cr(CNS)_6]_2$, etc., derivatives of the same acid, $H_3Cr(CNS)_6$, are also known.

We have succeeded in preparing a compound of vanadium analogous to this potassium salt, and find that it corresponds very closely to the latter in its reactions. The method employed was as follows:

[1] Ann. Chem. (Liebig), **3**, 163. [2] Rösler: *Ibid.*, **141**, 185.

An alcoholic solution of potassium sulphocyanate was made by fusing sulphur with potassium cyanide,[1] digesting the product with absolute alcohol, and filtering. To this solution was added somewhat less than the calculated quantity of vanadium chloride, dissolved in a small volume of water. A precipitate of potassium chloride at once appeared, and the solution assumed a deep brown color. After digestion for an hour on the water-bath, the solution was concentrated by evaporation, and then placed in a vacuum-desiccator to crystallize. The first crop of crystals consisted of a mixture of about equal proportions of potassium sulphocyanate and vanadisulphocyanate. This was removed, and the evaporation continued until the solution was of a thick, sirupy consistency. A large quantity of homogeneous, dark-red crystals, almost black, were thus obtained. They were cleaned as thoroughly as possible by pressure between filter-paper, washed with ether, and dried in a vacuum. The analysis gave the following results :

	Calculated for $K_3V(CNS)_6.4H_2O$.	Found.
K	19.90	19.52
C	12.24	....
N	14.29	14.73
S	32.65	33.23
V	8.68	8.55, 8.22, 8.79
H_2O	12.24	13.09
	100.00	

Potassium vanadisulphocyanate, like the corresponding chromium salt, is extremely soluble in both alcohol and water, but is stable only in presence of an excess of potassium sulphocyanate. The pure salt is decomposed by either solvent, forming a green solution. Crystals mixed with a small quantity of sulphocyanate are very hygroscopic, dissolving in the water absorbed. Toward oxygen the salt is the most stable of any which we have prepared. The vanadium in the radical $V(CNS)_6$ undergoes oxidation only very slowly, and in presence of potassium sulphocyanate the solution may be left exposed to the air for some time without losing its character-

[1] Chem. Zeitung, 1866, 666.

istic, dark-brown color. Alkalies precipitate vanadic hydroxide from the solution only on boiling, but it is at once decomposed by acids.

The preparation of corresponding salts of other metals, such as $Na_3V(CNS)_6$, $Ba_3[V(CNS)_6]_2$, etc., we have not yet attempted, but we hope to do so in the near future. Our investigations on the vanadic compounds in general will be continued.

NEW HAVEN, May, 1898.

THE CONDUCTIVITY OF AQUEOUS SOLUTIONS OF PRASEODYMIUM AND OF NEODYMIUM SULPHATES.

BY H. C. JONES AND H. M. REESE.

The salts used in this work were those which had been employed by one of us[1] in determining the atomic weights of praseodymium and of neodymium. The partly purified compounds were kindly furnished by Mr. Waldron Shapleigh. These were further purified by the method described in the article already cited, and, as there shown, the amount of impurities which remained in the compounds must have been small.

The solutions of the sulphates, which had been made from the oxides, in determining the atomic weights of the metals, were evaporated to dryness, and heated above the boiling-point of sulphuric acid, until constant weight was attained. The salts were then allowed to cool, in weighing-tubes with ground-glass stoppers, and from these sulphates the following solutions were prepared.

The water used had been purified from ordinary distilled water, by the method described by Jones and Mackay,[2] and was found to have an inappreciable conductivity.

In order to avoid the accumulative error which results from diluting a solution a large number of times, this was not repeated very often. A part of the original solution was diluted three or four times in succession, by removing a known volume from it, and adding a measured volume of water. The next dilution was prepared directly from the

[1] This JOURNAL, **20**, 345. [2] *Ibid.*, **19**, 91.

original solution, in a measuring-flask. This solution was then used as the starting-point in making the following three or four dilutions. The next more dilute solution was made directly from the original solution, and so on.

The Kohlrausch conductivity method, with Ostwald thermostat, was employed, and the cell standardized as usual with $\frac{N}{50}$-potassium chloride, which had been very carefully purified.

A solution of praseodymium sulphate was prepared containing 7.737 grams in 200 cc., which was equivalent to 38.685 grams to the liter. The molecular weight of praseodymium sulphate was taken as 569.1 ; hence the above solution was 0.06798 normal, or its volume was 14.71. From this solution all the more dilute solutions of this salt were prepared as already described.

The solution of neodymium sulphate which was prepared, contained 11.3595 grams in 500 cc. or 22.7190 grams in a liter. The molecular weight of neodymium sulphate was taken as 575.4, the volume of the above solution being then 25.326. From this, all the more dilute solutions were made.

The dilutions used, and the molecular conductivities found, for both salts, are given in the following table. v is the volume, or the number of liters which contains a gram-molecular weight of the salt, and μ_v, the molecular conductivities.

	Praseodymium sulphate.		Neodymium sulphate.	
	v	μ_v	v	μ_v
1	14.71	98.33	25.33	115.03
2	29.42	117.43	50.65	137.65
3	58.84	141.42	101.31	166.35
4	117.68	169.47	202.61	197.91
5	294.2	217.83	506.5	255.43
6	588.4	262.65	1013.0	303.45
7	1176.8	317.10	2026.0	366.0
8	1471.0	331.43	2532.6	382.9
9	2942.0	403.37	5065.2	462.5
10	5884.0	482.61		

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NOTE.

Liquid Hydrogen.

At the meeting of the Royal Society, on May 12, Professor Dewar contributed a preliminary note on the liquefaction of hydrogen and helium.

Professor Dewar said that in 1895 he described apparatus for the production of a jet of hydrogen containing liquid, and showed how such a jet could be used to cool bodies below the temperature that could be reached with liquid air, though all attempts to collect the liquid hydrogen failed. So far, no investigator had improved on the results described in 1895, and as the type of apparatus employed in those experiments worked well, it was resolved to construct a much larger liquid-air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen. The apparatus took a year to build up, and many months were occupied in testing and in making preliminary trials.

The many failures and defeats need not be detailed. On May 10 an experiment was started with hydrogen cooled to —205° C., and escaping continuously under a pressure of 180 atmospheres from the nozzle of a coil of pipe at the rate of 10 to 15 cubic feet a minute, in a vacuum vessel doubly silvered, and of special construction, surrounded with a space kept below —200° C. With these arrangements liquid hydrogen began to drop from this vacuum vessel into another, doubly isolated by being enclosed within a third, and in five minutes 20 cc. were collected. The hydrogen jet then froze up from the solidification of air in the pipes of the apparatus. The yield of liquid was about 1 per cent. of the gas. In the liquid condition the hydrogen was clear and colorless, showing no absorption-spectrum, and the meniscus was as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density must be in excess of the theoretical values; *viz.*, 0.18 to 0.12, deduced respectively from the atomic volume of organic compounds and the limiting density found by Amagat for hydrogen gas under infinite compression. Professor Dewar's old experiments on the density of hydrogen in palladium gave a value for the combined body of 0.62, and it would be interesting to find the real density of the liquid substance at its boiling-point. No arrangements being at hand to determine the boiling-point, two experiments were made to prove the excessively low temperature of the boiling fluid. In the first place, when a long piece of glass tubing, sealed at one end and open

to the air at the other, was cooled by immersing the closed end in the liquid hydrogen, the tube immediately filled, where it was cooled, with solid air.

The second experiment was with a tube containing helium.

The Cracow Academy Bulletin for 1896 contained a paper by Professor Olszewski entitled a "Research on the Liquefaction of Helium," in which he stated that, as far as his experiments went, helium remained a permanent gas, and apparently was much more difficult to liquefy than hydrogen. Professor Dewar, however, suggested that hydrogen and helium would probably be found to have about the same volatility, as was the case with oxygen and fluorine. Having a specimen of purified helium, extracted from Bath gas, sealed up in a bulb with a narrow tube attached, he placed the latter in the liquid hydrogen, whereupon a distinct liquid was seen to condense. From this result it would appear that there could not be any great difference in the boiling-points of hydrogen and helium.

In conclusion, Professor Dewar pointed out that all known gases had now been condensed into liquids which could be manipulated at their boiling-points under atmospheric pressure in suitably arranged vacuum vessels, though even so great a man as Clerk-Maxwell had doubts as to the possibility of ever liquefying hydrogen. With liquid hydrogen as the cooling agent, a temperature could be reached within 20° or 30° of the zero of absolute temperature, and its use would open up an entirely new field of scientific inquiry. No one could predict the properties of matter near that zero. Faraday liquefied chlorine in the year 1823. Sixty years afterwards, Wroblewski and Olszewski produced liquid air, and now, after an interval of fifteen years, the remaining gases—hydrogen and helium—were obtained as static liquids Considering that the step from the liquefaction of air to that of hydrogen is relatively as great in a thermodynamic sense as that from liquid chlorine to liquid air, the fact that the former had been achieved in one-fourth the time needed to accomplish the latter proved the greatly accelerated rate of scientific progress in the present age.

The paper ended with an acknowledgment of the aid rendered by Mr. Robert Lennox, without whose engineering skill, manipulative ability, and loyal perseverance, the present successful issue might have been indefinitely delayed.—*Chemical News.*

REVIEWS.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. By Dr. ALEXANDER CLASSEN in cooperation with Dr. WALTER LÖB. Authorized translation, third English, from the revised and greatly enlarged fourth German edition, by W. H. HERRICK and B. B. BOLTWOOD. John Wiley & Sons, New York, and Chapman & Hall, London, 1898.

Repeated issue of new editions, both in German and English, of this useful manual testify to the appreciation which it has deserved and received. It has clearly taken its place as one of the standard volumes needed in a working collection of books on analytical chemistry. The principal expansion made, in the fourth German edition, of the work in its earlier form is an extended chapter on the theory of electrolysis, with detailed explanations in regard to the bearing of electrode tension, current strength and decomposition tension on the practical results aimed at. This has added materially to the value of the book as a systematic treatise, and the carefully worked over matter on the several determinations of individual metals will enable anyone to apply the electrolytic method most satisfactorily to each particular purpose.

The special examples of crude materials for analysis and their treatment—omitted from the fourth German edition, but included by the translators in the form of an appendix—embrace some cases for which the (partial) applications of electrolytic methods must be regarded rather as *tours de force* than as practically useful processes.

A good feature of the book is the abundant references to original papers, in which the details of methods, and the reasons for them, may be fully traced. J. W. M.

VORLESUNGEN ÜBER THEORETISCHE UND PHYSIKALISCHE CHEMIE. Von J. H. VAN 'T HOFF. Erstes Heft; DIE CHEMISCHE DYNAMIK. Mit in den Text eingedruckten Abbildungen. Druck und Verlag von Friedrich Vieweg und Sohn. 1898. pp. 252.

This book is based upon the course of lectures given by its author in the University of Berlin, on "Selected Chapters in Physical Chemistry."

The order of treatment which Van't Hoff prefers and adopts is: First, Chemical Dynamics; Second, Chemical Statics; Third, Relation between Properties and Composition.

The first number, which is now at hand, deals only with questions in Dynamics, and under the two general divisions of Chemical Equilibrium and Reaction Velocity. Among the problems in equilibrium which are discussed, are: Physical and chemical equilibria between two, three, and four substances, and chemical equilibrium from the point of view of molecular mechanics, including homogeneous and heteroge-

neous equilibria. The subject of velocity of reactions is considered under the heads: Reaction-velocity and equilibrium; the kinetics of reaction, including mono-, di-, and trimolecular reactions; empirical conditions which affect the velocity of reactions; effect of temperature on the velocity of reactions; etc.

The work is appearing at the same time as that portion of Ostwald's *Lehrbuch* (*Verwandschaftslehre*) which deals with many of the same problems, and all who are interested in physical chemistry will regard it as particularly fortunate, that they are furnished simultaneously with two such masterpieces from the hands of the two great leaders in this field.

H. C. J.

REPERTORIUM DER TECHNISCHEN JOURNAL-LITTERATUR. Herausgegeben im Kaiserlichen Patentamt. Jahrgang: 1896. Berlin: Carl Heymanns. Verlag: 1897.

This work is well described in the title. It is characterized by German thoroughness, and while of course it is impossible for the reviewer to verify many of the references, it is fair to assume that it is a reliable guide. It would seem to be indispensable to all who are interested in technical literature. No less than 261 journals are included in the list of those which are referred to in the book. An examination of this list shows clearly, as might have been expected, that nothing of importance is omitted from it. The classification of subjects seems to be a convenient one, and further, there is a full index which will much facilitate the finding of any particular article that may be wanted.

ANIMAL FATS AND OILS, their practical production, purification and uses for a great variety of purposes, their properties, falsification and examination. BY LOUIS EDGAR ANDÉS, translated by CHARLES SALTER. Scott, Greenwood & Co., London, 1898.

In this not very large volume, of 231 pages, may be found a good deal of information as to the practical methods of treating animal fats on the industrial scale, the mechanical arrangements for cutting up and "rendering" the crude material, the melting pans, presses, etc., including contrivances intended to diminish the annoyance and improve the sanitary relations of bone-boiling and other offensive branches of the business. The account of recent arrangements for using carbon tetrachloride as a solvent for the extraction of fat is interesting, among the advantages of this solvent being the evident one of its not being inflammable.

A good many expressions are to be found which are open to criticism as more or less inaccurate from a scientific standpoint—*e.g.*, on p. 1 it is said of animal fats, "they are, almost exclusively, compounds of one or frequently several, fatty

acids with glycerine ethers"—on pp. 4 and 179 spermaceti and sperm oil and seal oil are classed under the head of "fish oils"—on p. 11 the formula for oleic acid is given as $C_{19}H_{18}O_2$—on p. 113 it is stated that by steaming bones a large portion of the "cartilage" is dissolved. Objection may be made to a phrase here and there as not quite defensible English, as on p. 10, "soluble in hot alcohol, ether, benzene, petroleum ether, etc. (at least *in the warm*)", and on p. 21, "oil- and fat-producing seeds and fruits will bear *any length of transport*." The discussion of wool-fat is limited to the organic constituents of "*suint*," no mention being made of the production from it of potash. Statements are repeatedly made in the body of the work as to the results of the examination of individual fats, under such heads as "Reichert number," "Hehner number," "iodine number," etc., without any explanation of the meaning of these terms, such explanation being given only in very condensed form in two or three pages at the very end of the volume.

For the general chemistry of animal (and other) fats, and especially for full details as to their examination by chemical and physical means, several books published within the last few years are much to be preferred—such as F. Jean: Chimie Analytique des Matières Grasses, Paris, 1892; R. Benedikt: Analyse der Fette und Wachsarten, Berlin, 1892; and C. R. Alder Wright: Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes, London, 1894. This last-named work also gives much information as to industrial processes and plant.

J. W. M.